PB86-114071

Lead-Poisoned Catalyst Evaluation

Southwest Research Inst., San Antonio, TX

Prepared for

Environmental Protection Agency, Ann Arbor, MI

Aug 85

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA

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1. REPORT NO. EPA 460/3-84-007	2.	3. RECIPIENT'S ACCESSION NO. PB8 6 114071/AS
4. TITLE AND SUBTITLE Lead-Poisoned Catalyst Evaluation		5. REPORT DATE August 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E. Robert Fanick Melvin N. Ingalls		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute Department of Emissions Research 6220 Culebra Road San Antonio, Texas 78284		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-03-3162
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency 2565 Plymouth Road Ann Arbor, Michigan 48105		13. TYPE OF REPORT AND PERIOD COVERED Final (Feb. 1984 - June 1984)
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Ten catalyst from eight vehicles representing four vehicle manufacturers were examined using several physical and chemical procedures for poison accumulation, overheating, plugging, thermal deterioration, and noble metal loss. The analysis of each converter consisted of visual inspection, whole converter radiographs BET surface area, elemental analysis, and scanning electron microscope examination of surface. Correlations between the "on-vehicle" emissions and the analytical results were conducted.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Exhaust Emissions Motor Vehicles	Catalyst, lead poisoned, intentionally leaded catalyst, leaded fuel, poison accumulation catalyst deterioration	

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 149
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $16.95

EPA Form 2220-1 (9-73)

PB86-114071

United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-84-007
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Air

EPA

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA 460/3-84-007

Lead-Poisoned Catalyst Evaluation

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Work Assignment 17

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Publication No. EPA-460/3-84-007

FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research at Southwest Research Institute (SwRI). It was begun in February 1984, and completed in June 1984. The project was conducted under Work Assignment 17 of Contract 68-03-3162, and was identified within Southwest Research Institute as Project 03-7338-017.

Mr. Robert J. Garbe of the Emission Control Technology Division, Office of Mobile Source Air Pollution Control, Environmental Protection Agency, Ann Arbor, Michigan, served as EPA Project Officer for most of the project. Mr. Craig Harvey of the same EPA Office served as Project Officer for the last stages of the project. Mr. R. Bruce Michael, Emission Control Technology Division, Office of Mobile Source Air Pollution Control, EPA, Ann Arbor, Michigan was the Branch Technical Representative for the project. Mr. Charles T. Hare, Manager, Advanced Technology, Department of Emissions Research, Southwest Research Institute, served as the Project Manager. E. Robert Fanick, Research Scientist, served as Project Leader and Principal investigator. Other key personnel at SwRI involved in the project were Ms. Karen B. Kohl, who supervised the x-ray fluorescence analysis, Mr. James G. Barbee, who supervised the scanning electron microscope, and Mr. Edward H. Ruescher, who supervised the whole catalyst x-ray analysis. The support personnel at SwRI involved in this program included Dennis M. Lovell, A. Joyce Winfield, Pam Nickoloff, James G. Herrera and O.C. Skiles.

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SUMMARY

The purpose of this project was to provide the Environmental Protection Agency (EPA) with information which could be used in conjunction with EPA emission test data to evaluate the relationship between catalyst condition and emission levels. The catalysts evaluated in this program had been intentionally poisoned with known amounts of leaded gasoline. The catalysts represent four different vehicle manufacturers from eight different vehicles with three-way catalyst technology.

Ten catalysts were examined using several physical and chemical procedures for poison accumulation, overheating, plugging, thermal deterioration and noble metal loss. The analysis of each catalyst consists of external visual inspection, whole converter radiographs, internal visual inspection, weighing of catalysts, BET surface area analysis, elemental analysis for noble metals and poisons, and scanning electron microscope examination of the surface.

Whole converter radiographs (x-rays) of the converters were performed to check for cracks, voids, meltdowns, and lead distribution prior to disassembly of the converter.

The converters showed an interesting correlation between the concentration of lead (measured by x-ray fluorescence) and the film negative opacity using the whole converter radiographs. As the lead concentration in each biscuit increased, the opacity of the radiographs decrease.

During disassembly, visual inspections were performed for evidence of physical damage, plugging, overheating, and the evaluation of discoloration and deposit patterns. Samples of the catalytic material were taken for BET surface analysis, elemental analysis by x-ray fluorescence, and examination with a scanning electron microscope. The results from all of the analyses for each catalyst are presented for comparison purposes.

The elements quantified by x-ray fluorescence were phosphorus (P), sulfur (S), calcium (Ca), manganese (Mn), zinc (Zn), lead (Pb), platinum (Pt), palladium (Pd), nickel (Ni), and rhodium (Rh). In general, the Ni and Pb concentrations were higher on the first biscuit and S concentration was higher on the second biscuit. Most of the biscuits contained both Pt and Pd. Cerium (Ce), titanium (Ti) and iron (Fe) were found in many of the converters.

The catalyst surface of the upstream biscuits when observed through a scanning electron microscope had the appearance of very fine grains spread evenly over the surfact. The downstream biscuits had the appearance of dried cracked mud. All of the micrographs were taken at the magnification of X500.

A short statistical analysis was performed to examine the correlation between the analytical results and/or the emission levels. The best linear correlations, in terms of the analytical results only, were between Zn and P, Zn and Ca, and Ni and S. the Ni/S correlation was an increase relation (i.e. an increase in S results in a decrease of Ni and vice versa). Another linear

correlation was conducted for the average weight percent of the elements in each container, the percent change in the emissions, and the fuel lead put through the vehicle. The fuel lead correlated with P and Zn, and the hydrocarbons and oxides of nitrogen correlated with S. A moderate correlation existed between CO and Pb. It is not possible to draw conclusions regarding any relationship between the lead retained in the converters and the increase in vehicle emission levels with the limited catalyst sample examined. The evaluation of additional catalysts would be necessary to determine any relationship between these variables.

I. INTRODUCTION

Since 1975, exhaust gas catalytic converter systems have been the principal means of automotive pollution control. The catalytic activity of the converter can be degraded by engine and emission control system malfunctions and by the use of leaded fuel. This project examined a number of catalytic converters in an effort to describe the physical condition of the catalytic material after exposure to known amounts of leaded gasoline.

This examination included radiographs of whole monolithic catalysts for cracks, voids, and meltdowns; visual inspection of the converters as they were disassembled; and weighing of the catalytic material. Several physical and chemical analytical procedures were performed to further define the condition of the catalyst. These procedures included BET surface area, elemental analysis by x-ray fluorescence, and surface examination using a scanning electron microscope.

The purpose of this project was to provide the EPA with information on the condition of each catalyst. This information included examination for poison accumulation, overheating, plugging, thermal deterioration, and noble metal loss. The EPA will use this information, together with the results from emissions tests on the vehicles from which these converters were taken, in an effort to correlate emission test results with catalyst condition and lead loading. A description of each of the procedures is included in Appendix A.

For the purpose of identifying the converters analyzed in the program, each converter will be designated by the three digit EPA vehicle number on the vehicle from which the converter was removed. In the event of a dual converter vehicle, the converters were also identified -1 and -2 after the three digit vehicle number. No means were available to determine where the converter was located on the vehicle (i.e. right bank or left bank of the engine); therefore, these numbers are arbitrary. The term "biscuit" will be used to refer to each individual piece of monolithic catalyst material in a converter. In the case of two "biscuit" converters, the upstream biscuit was labeled "A" and the downstream biscuit was labeled "B".

II. BACKGROUND

The converters were obtained from EPA and were collected from four different misfueling programs. Three of those programs were conducted by an EPA contractor, Automotive Test Laboratory (ATL) in Ohio, and one was conducted "in-house".(1) Each program utilized a different method of misfueling the vehicle. Table 1 identifies the converters selected for this program and the source and type of misfueling. In all cases, the converters were removed for future analysis and new converters were placed on the vehicles.

TABLE 1. SELECTED CONVERTERS FROM EPA MISFUELING PROGRAMS

Vehicle	Program	MYR	MFR	Eng. Fam	Fuel Lead Grams	Approximate # of tankfuls of leaded fuel
002	ATL #1	81	Ford	1.6AP	88.9	10
004	ATL #1	81	VW	BVW1.7V6 FF537F	93.0	10
304[a]	ATL #5	82	Ford	CFM5.0V2 HDF8	201.5	12
307	ATL #5	83	GM	DIG3.8V2 NDA4	105.2	12
309	ATL #6	83	Chrysler	DCR2.2V2 HAC3	56.2	4
310[a]	ATL #5	83	Ford	DFM5.0V5 HLF8	76.7	4
312	ATL #6	82	GM	CIG5.0V5 NBM2	66.2	4
941	In-House	83	GM	DIG2.8V2 NNA9	60.0	4

[a] Dual converters

---

*Numbers in parentheses refer to references at the end of this report.

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Test Programs

In the first program (ATL #1), the effect on emissions from misfueling vehicles with 10 tankfuls of leaded fuel was investigated. Each vehicle met several criteria:

1. 1981 with 25,000 miles or 1982 with 15,000 miles
2. Less than 0.05 g per gallon lead used previously
3. Tailpipe checked for lead-negative
4. Vehicles require only minor adjustments to manufacture specification
5. No vehicle with emission levels more than 50% above FTP certification standards
6. All mileage accumulated during the program on a track

All emission tests were performed with Indolene unleaded gasoline and the emission tests were conducted after every two tanks. The leaded fuel for all vehicles was to be from one source and have between 1.09 and 0.98 g lead per gallon. Two converters were obtained from this program (Ford-002 and VW-004).

The second program (ATL #5) involved misfueling during approximately one out of every two tanks. The same criteria applied to this program with these changes:

1. 1981-1983 model years
2. Closed-loop, three-way catalyst (with or without additional oxidation catalyst) system
3. 4000 odometer miles or greater
4. No two engine families alike
5. All mileage accumulation performed during the program in normal driving on public roads
6. Unleaded fuel for mileage accumulation from commercial sources.

Two converters were obtained from this program (Ford-304 and GM-307).

The third program (ATL #6) involved criteria similar to ATL #5 except that the vehicles were misfueled approximately one out of every four tanks and the mileage accumulation consisted of a one-hour road route at an average speed of 32 mph. All unleaded fuel purchases were to be made at a designated service station on the road route where the lead content of the station fuel tank was checked at least once each week. Three converters were obtained from this program (Chrysler-309, Ford-310, and GM-312).

The fourth program was an EPA in-house intermittent misfueling program. Criteria similar to the previous programs were used. The major difference involved the casual or intermittent misfueling of the vehicle. Using the composite city/highway fuel economy, the approximate mileage per tankful was calculated. The vehicle was then misfueled after more than three tanks of unleaded fuel were used on the basis of the mileage calculation. One converter was provided for analysis from this program (GM-941).

Emission Results

Results of emission tests conducted during the four programs were provided to SwRI by EPA. The initial emission test was conducted on each vehicle before misfueling, and the final emission test was the last test after all of the misfueling and mileage accumulation had been completed. Table 2 shows the results of these tests on each vehicle. All emission tests in this table are from a cold-start Federal Test Procedure (CFTP) using unleaded Indolene gasoline. The emission trends are presented in Figures 1 through 3. In general, all of the final emissions were higher than the initial values with exception of the NO_x for vehicles 304 and 309.

TABLE 2. EFFECT OF MISFUELING ON EXHAUST EMISSIONS

Vehicle	Total Fuel Grams	CFTP Emissions		
		HC	CO	NO_x
002	Initial	0.57	11.80	0.59
	88.9	2.14	39.60	0.82
004	Initial	0.33	2.01	0.98
	93.0	1.40	2.24	1.98
304	Initial	0.75	11.44	0.84
	201.5	3.64	30.32	0.82
307	Initial	0.22	1.33	0.79
	105.2	1.41	2.62	1.33
309	Initial	0.40	4.12	1.00
	56.2	1.29	5.92	0.83
310	Initial	0.37	5.40	0.68
	76.7	1.34	6.33	1.15
312	Initial	0.40	4.84	0.54
	66.5	0.71	5.34	0.79
941	Initial	0.17	1.66	0.92
	60.0	0.58	3.25	1.00

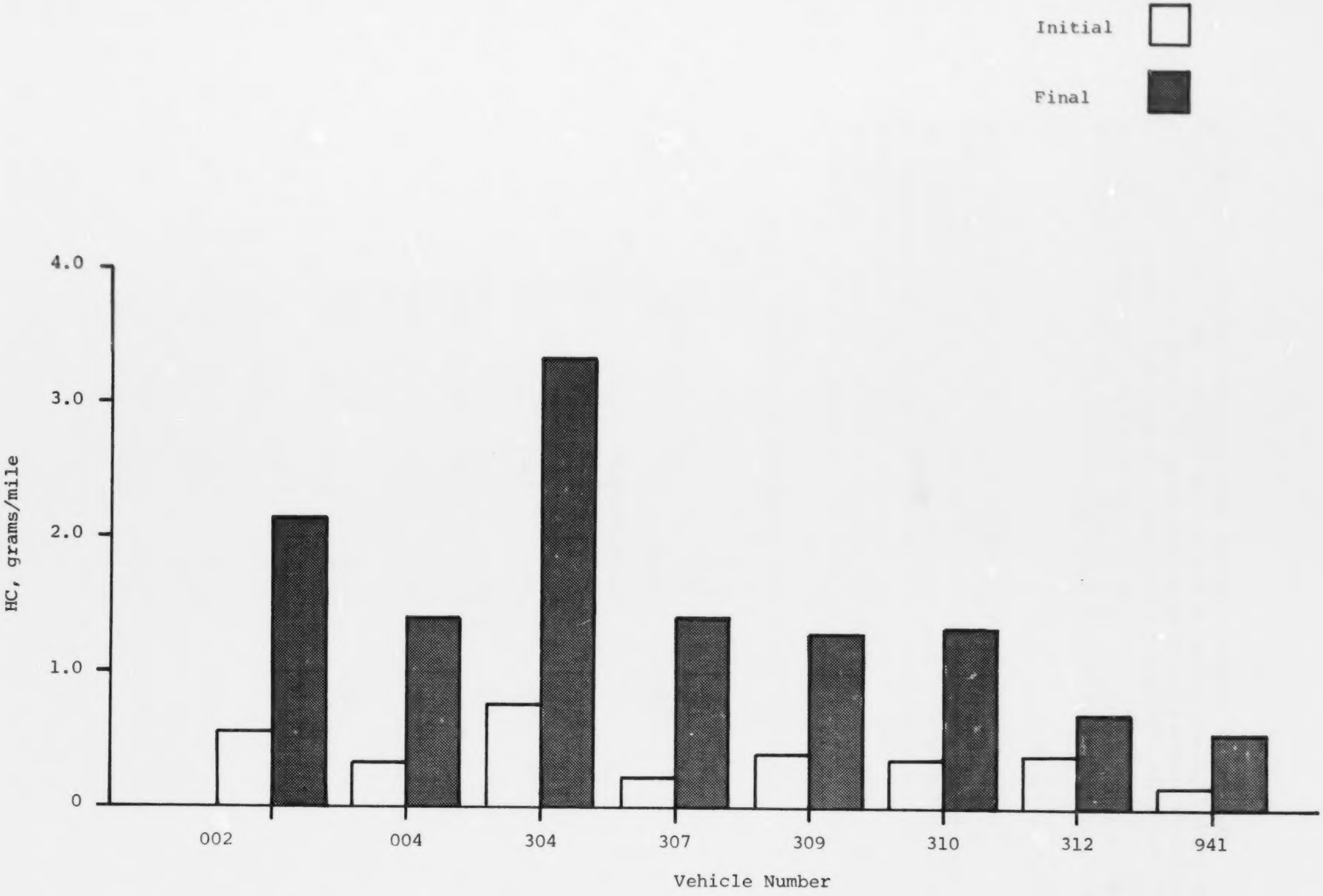

Figure 1. Initial and final FTP results from misfueled vehicles (hydrocarbons)

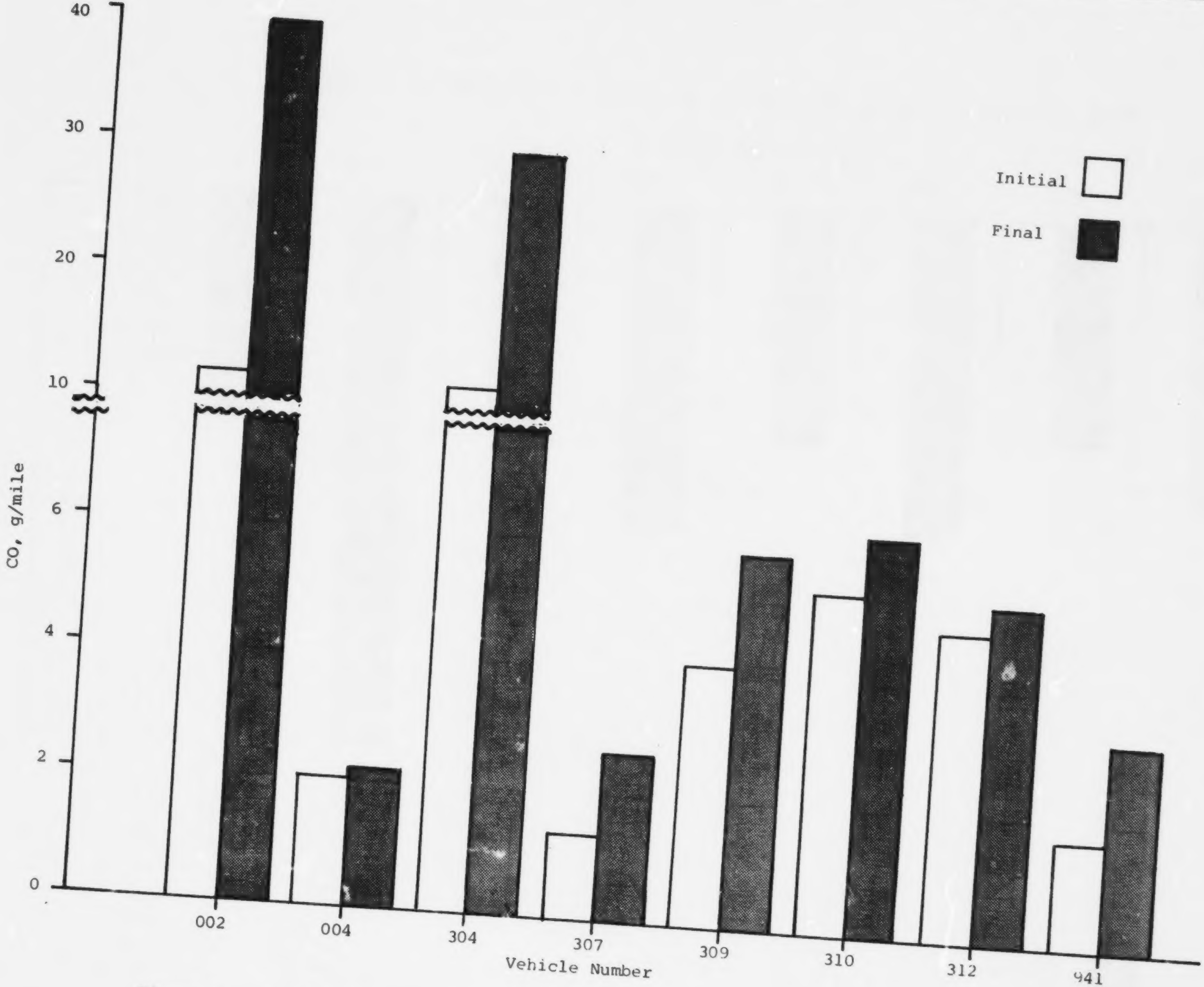

Figure 2. Initial and final FTP results from misfueled vehicles (carbon monoxide)

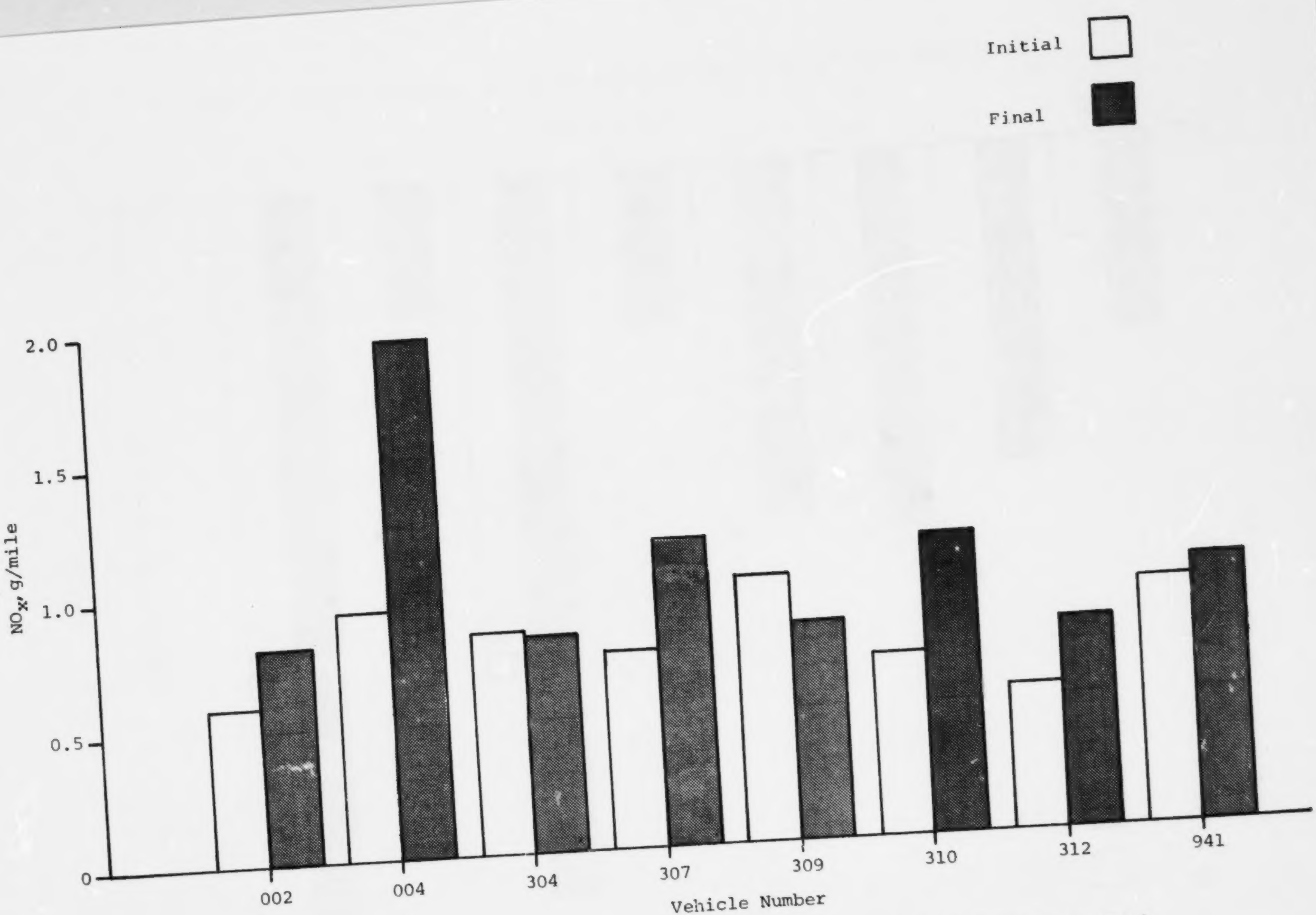

Figure 3. Initial and final FTP results from misfueled vehicles (NO_x)

III. WHOLE CONVERTER RADIOGRAPH

A whole converter radiograph was obtained for each converter. This served two major purposes: to determine internal structural damage, overheating, etc.; and to assist in opening the container without damaging the biscuits. A description of the procedures used in conducting the analysis is included in Appendix A, and the radiographs of each converter when lying flat are shown in Appendix B.

In general, the radiographs do not provide a significant amount of quantitative data. Cracks were observed in both biscuits of 307 and 312. A large section of the front face of 312 was shown to be missing. This piece did not appear to be lodged in another part of the container. A dark band was also observed on the upstream edge of A biscuit for each converter. This is presumably from a high concentration of lead deposition. Converters 002 and 309 also show a dark band on the upstream side of the B biscuit.

In an attempt to correlate these light and dark regions, a densitometer was employed with the negatives. Eight locations each on the upstream and downstream side of each biscuit were examined with the densitometer (See Figure 4). On the photographic negative, a lower number indicates more lead (i.e., less film exposure to the x-rays or more x-rays absorbed by lead). This translates to a dark region in the positives shown in Appendix B. The results from the densitometer are presented in Table 3. The film density is defined as the logarithm of the opacity or the logarithm of the reciprocal of the transmittance of the light through the film. Transmittance is defined as:

$$\text{Transmittance} = \frac{\text{Transmitted light}}{\text{Incident light}}$$

Opacity is defined as:

$$\text{Opacity} = \frac{1}{\text{Transmittance}}$$

and

$$\text{Density} = \log \text{Opacity} = \log \frac{1}{\text{Transmittance}}$$

The density of the image on the negative depends on the length of the exposure, thickness of the container, energy of the x-rays, and the angle of the converter with respect to the film. Figure 5 was plotted from the average densitometer values taken from the upstream portion of each biscuit. In general, the graph illustrates the correlation of the lighter areas from the radiographs with the mass of lead in each whole biscuit obtained from the x-ray fluorescence (i.e., the highest concentration of the lead deposits is located on the upstream portion of each biscuit). The one converter that did not fit the trend was the VW converter 004 (identified in Figure 5). This converter was irradiated for a longer time because it had a much thicker container than the other converters. As a result of the longer irradiation time and the thicker container, the actual densitometer values for this converter will be different. If the values are then normalized to account for these differences a linear relationship between the film density and lead concentration should result.

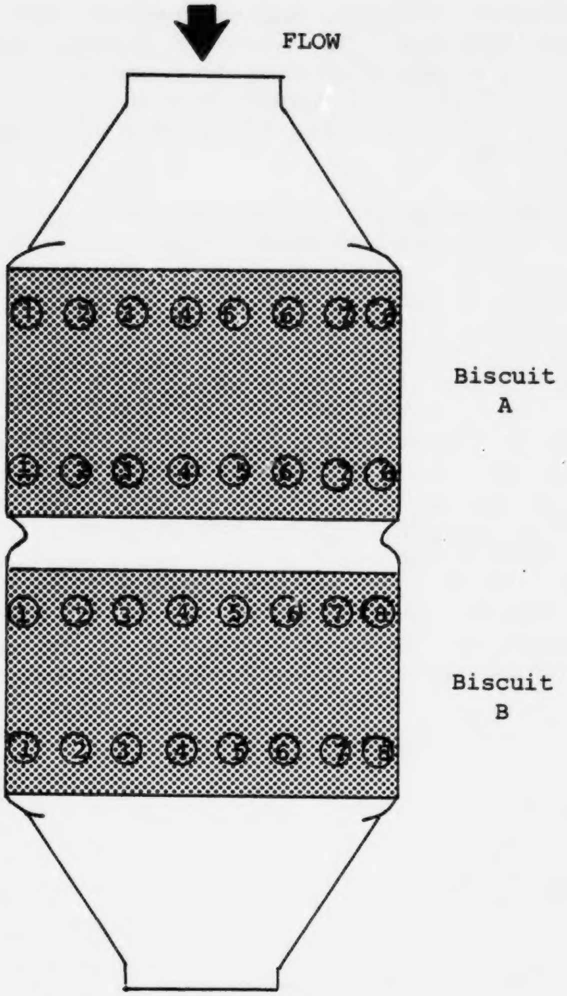
FLOW
1
2
3
4
5
6
7
8
Biscuit
A
Biscuit
B

Figure 4. Locations of densitometer readings

TABLE 3. DENSITOMETER VALUES FROM WHOLE CONVERTER RADIOGRAPHS

Catalyst No.	Biscuit No.	Film Density at Position									
		1	2	3	4	5	6	7	8	Avg.	Pb. g
002	A-Front	0.80	0.50	0.40	0.36	0.38	0.50	0.72	0.72	0.55	12.762
	A-Back	0.93	0.83	0.83	0.75	0.61	0.67	0.93	0.98	0.82	
	B-Front	1.07	0.69	0.59	0.63	0.63	0.65	0.68	0.99	0.74	8.351
	B-Back	1.05	1.19	1.10	0.92	0.84	0.96	1.09	1.12	1.03	
004	Front	1.14	0.78	0.59	0.49	0.56	1.03	--	--	0.77	21.448
	Middle	1.02	0.81	0.67	0.63	0.57	1.17	--	--	0.81	
	Back	1.05	0.90	0.82	0.81	0.75	1.28	--	--	0.94	
304-1	A-Front	0.93	0.61	0.51	0.50	0.47	0.45	0.47	0.59	0.57	11.243
	A-Back	1.03	1.21	1.24	1.12	1.12	1.13	1.27	1.09	1.31	
	B-Front	0.94	1.01	1.39	1.25	1.39	1.25	1.35	1.15	1.22	5.905
	B-Back	1.10	1.38	1.61	1.39	1.35	1.32	1.27	1.09	1.31	
304-2	A-Front	0.70	0.52	0.50	0.52	0.61	0.56	0.66	0.83	0.61	13.094
	A-Back	1.21	1.44	1.39	1.50	1.46	1.48	1.39	1.17	1.38	
	B-Front	1.23	1.35	1.23	1.25	1.27	1.19	1.01	1.10	1.20	5.998
	B-Back	1.32	1.30	1.25	1.27	1.32	1.39	1.32	1.09	1.27	
307	A-Front	1.02	0.82	0.68	0.61	0.67	0.66	0.73	0.86	0.76	15.201
	A-Back	1.01	1.19	1.14	1.16	1.10	1.17	1.14	1.06	1.12	
	B-Front	0.94	1.07	1.04	1.03	1.25	1.14	1.03	0.90	1.05	10.665
	B-Back	1.09	1.14	1.16	1.09	1.47	1.11	1.19	1.02	1.16	
309	A-Front	1.01	1.04	0.91	0.89	0.83	0.85	0.88	0.96	0.92	7.552
	A-Back	0.88	0.98	0.89	0.97	0.96	0.93	0.92	0.82	0.92	
	B-Front	0.80	0.69	0.63	0.58	0.60	0.61	0.73	0.90	0.69	11.071
	B-Back	1.02	1.06	0.95	0.93	0.91	0.97	1.06	1.16	1.01	
310-1	A-Front	1.00	0.90	0.81	0.80	0.77	0.89	0.87	0.92	0.87	8.404
	A-Back	1.21	1.25	1.14	1.09	1.05	1.10	1.13	1.02	1.12	
	B-Front	1.24	1.37	1.49	1.52	1.48	1.29	1.40	1.40	1.40	4.519
	B-Back	1.16	1.21	1.11	1.10	1.27	1.22	1.15	1.21	1.18	
310-2	A-Front	0.94	0.92	0.82	0.78	0.76	0.82	0.89	1.02	0.87	8.025
	A-Back	1.22	1.28	1.48	1.27	1.38	1.42	1.32	1.17	1.32	
	B-Front	1.22	1.40	1.30	1.41	1.41	1.35	1.35	1.33	1.35	3.084
	B-Back	1.53	1.68	1.71	1.88	1.84	1.61	1.70	1.57	1.69	
312	A-Front	1.02	0.97	0.87	0.78	0.84	1.03	0.99	1.22	0.97	10.807
	A-Back	1.11	1.36	1.42	1.35	1.40	1.44	1.33	1.19	1.33	
	B-Front	1.16	1.50	1.50	1.47	1.63	1.44	1.47	1.24	1.43	4.934
	B-Back	1.12	1.48	1.52	1.57	1.67	1.41	1.35	1.20	1.42	
941	A-Front	0.89	0.69	0.57	0.53	0.50	0.56	0.61	0.70	0.63	17.201
	A-Back	1.00	1.22	1.18	1.05	1.11	1.20	1.18	1.06	1.13	
	B-Front	1.11	1.24	1.38	1.40	1.36	1.28	1.38	1.23	1.30	3.848
	B-Back	1.04	1.38	1.35	1.31	1.19	1.20	1.33	1.26	1.26	

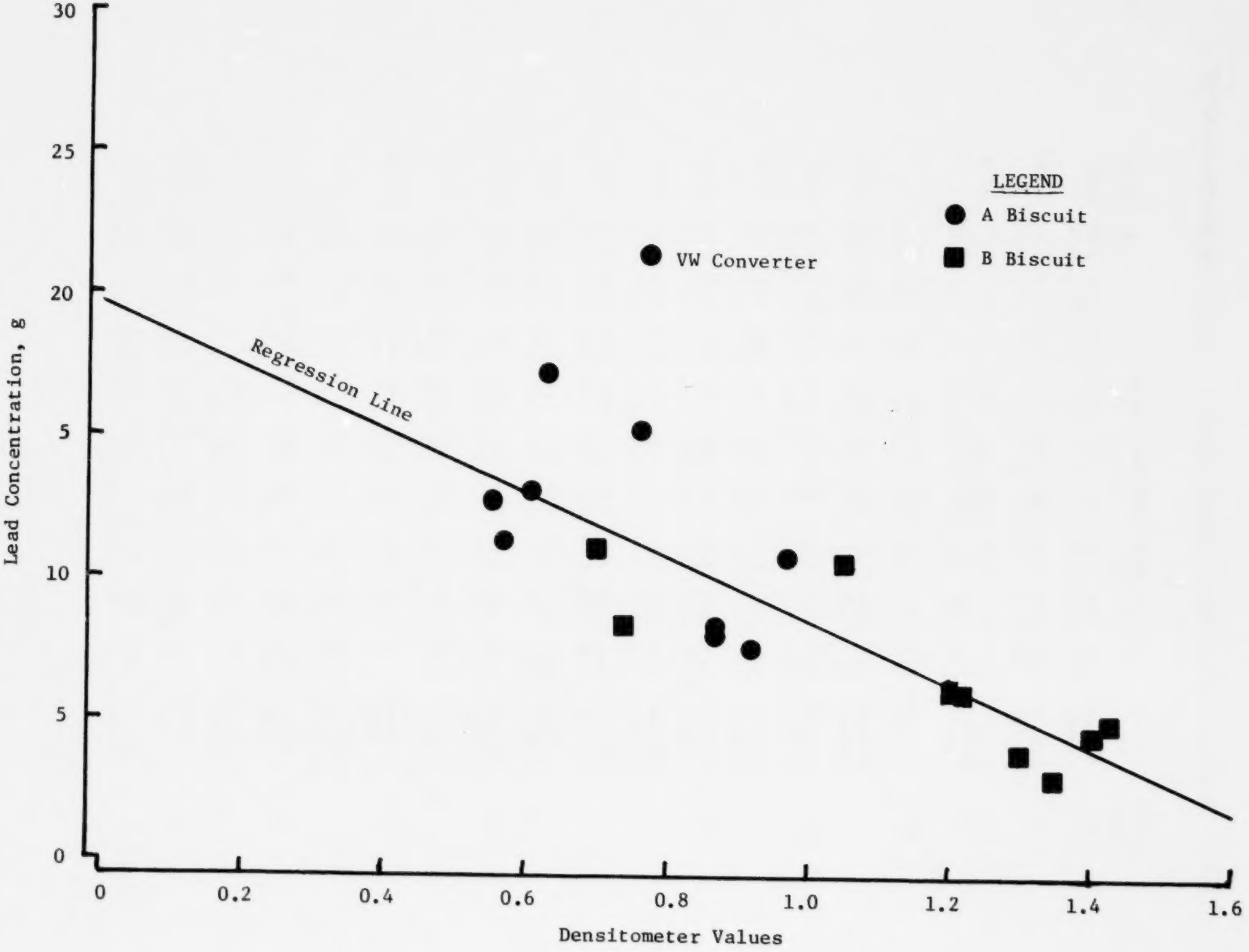

Figure 5. Plot of densitometer values versus lead concentration per biscuit

IV. VISUAL INSPECTION AND WEIGHING

Each converter was photographed both externally and internally. The photographs of all the converters are shown in Appendix C. In general, the external and internal views for each manufacturer's converters are similar.

The weights of the converters were determined in various stages. All converters were shipped to SwRI with the mounting brackets and heat shields intact except for 004, 310-1, and 310-2. Each converter was weighed with and without the mounting brackets and heat shields. Once the containers were opened, the individual biscuits were reweighed. All these weights are presented in Table 4.

TABLE 4. CONVERTER WEIGHTS

	Whole Converter		Biscuits	
Converter Number	With Mounting Brackets, lb	Without Mounting Brackets, lb	Upstream-A, g	Downstream-B, g
002	10.76	7.18	402.6	372.8
004		5.80	936.6	--
304-1	11.68	8.97	493.1	444.0
304-2	11.88	8.95	471.0	451.0
307	11.95	10.93	894.2	725.5
309	10.51	9.86	1110.6	477.2
310-1		8.85	390.9	451.9
310-2		8.95	393.4	411.2
312	11.95	10.83	831.3	715.1
941	11.75	10.67	945.1	726.1

In general, the weights for each biscuit from individual manufacturers are very similar. Both biscuits in Ford converters weigh approximately 400 g. In the case of GM converters, the upstream biscuit is more than 100 g heavier than the downstream biscuit. With Chrysler converters, the upstream biscuit is more than twice as heavy. The VW converter was the only single-biscuit converter in this study. No comparisons were made in the converter weights between clean, unused converters and the intentionally leaded converters from this program.

Three converters showed internal structure damage to the substrate material upon opening the container. These converters were 307, 310-2 and

312. Two of the three GM converters (307 and 312) were cracked perpendicular to the flow of the exhaust. Each biscuit in each container was cracked almost exactly in half. These converters were either damaged during the manufacturing or possibly overheated during use. In addition, a large section from the front face of the upstream biscuit was missing from 312. The damage to 310-2 consisted of a section missing from the edge of the front face of the B biscuit. No traces of the pieces were found for either of these converters, so it was presumed that the pieces were missing at the time the converters were installed by the vehicle manufacturer or lost upon removal from the vehicle. All of the other converters were intact and showed no signs of overheating or internal damage. The internal examination of each converter verified the observation from the whole catalyst radiographs. Upon close inspection, all of the converters consisted of square cells, with the exception of the Chrysler converter, which had triangular cells. In general the upstream face of each biscuit was darker in color (dark gray to black) than the downstream face of the same biscuit. Only 002 and 941 showed any appreciable amount of plugging of the upstream biscuit. Converters 002 and 004 were the lightest in color. These two converters were from the program which misfueled vehicles continuously, ATL #1.

V. SURFACE AREA BY BET ANALYSIS

The specific surface area of each biscuit was determined by Micromeritics Instrument Corporation using the BET method. A description of the sampling and analysis procedure is presented in Appendix A. The computer printouts and raw data provided by Micromeritics are presented in Appendix C.

In general, the specific surface areas for converters 002 and 004 were less than the other converters with the exception of 309, 312, and the B biscuit of 304-2. Converters 002 and 004 were misfueled with 10 tankfuls of leaded fuel and did not have a chance to "burn off" the deposits with any unleaded fuel between misfuelings. Converter 312 was one of the converters that had a number of structural fractures perpendicular to the flow of the exhaust. Each biscuit was cracked to tow almost equal pieces. The cracks, combined with the low specific surface area, may indicate that this catalyst had been overheated. All of the other converters had a specific surface area greater than 10 m^2/g. The overheating of the converter could also be verified by a technique call x-ray diffraction. This technique determines the change in alummina crystal structure caused by overheating. In many uses the overheating of the catalyst lowers the surface area of a catalyst.

The specific surface area data for each converter are presented in Table 5 and illustrated in Figure 6. Two of the three GM converters had the highest surface area (307 and 941) but the lowest surface area was also a GM (312). No data were available to draw conclusions about the change in surface area due to lead deposition in comparison with clean, unused converters. The effective surface area for gamma alumina is typically on the order of 100-200 m^2/g.(2) The total surface area of a biscuit depends on the volume (size) of the biscuit, the cell size of the biscuit and the thickness of the wash coat.

TABLE 5. CATALYST SPECIFIC SURFACE AREA

Biscuit Number	Surface Area	
	Specific, m^2/g	Total, m^2
002-A	9.6	3,856
002-B	4.4	1,640
004	6.0	5,620
304-1-A	10.3	5,079
304-1-B	13.6	6,038
304-2-A	12.7	5,982
304-2-B	4.4	1,984
307-A	22.9	20,477
307-B	19.2	13,930
309-A	7.7	8,552
309-B	5.4	2,577
310-1-A	18.2	7,114
310-1-B	17.5	7,908
310-2-A	16.1	6,334
310-2-B	16.1	6,620
312-A	1.5	1,242
312-B	5.5	3,933
941-A	18.4	17,390
941-B	24.1	17,499

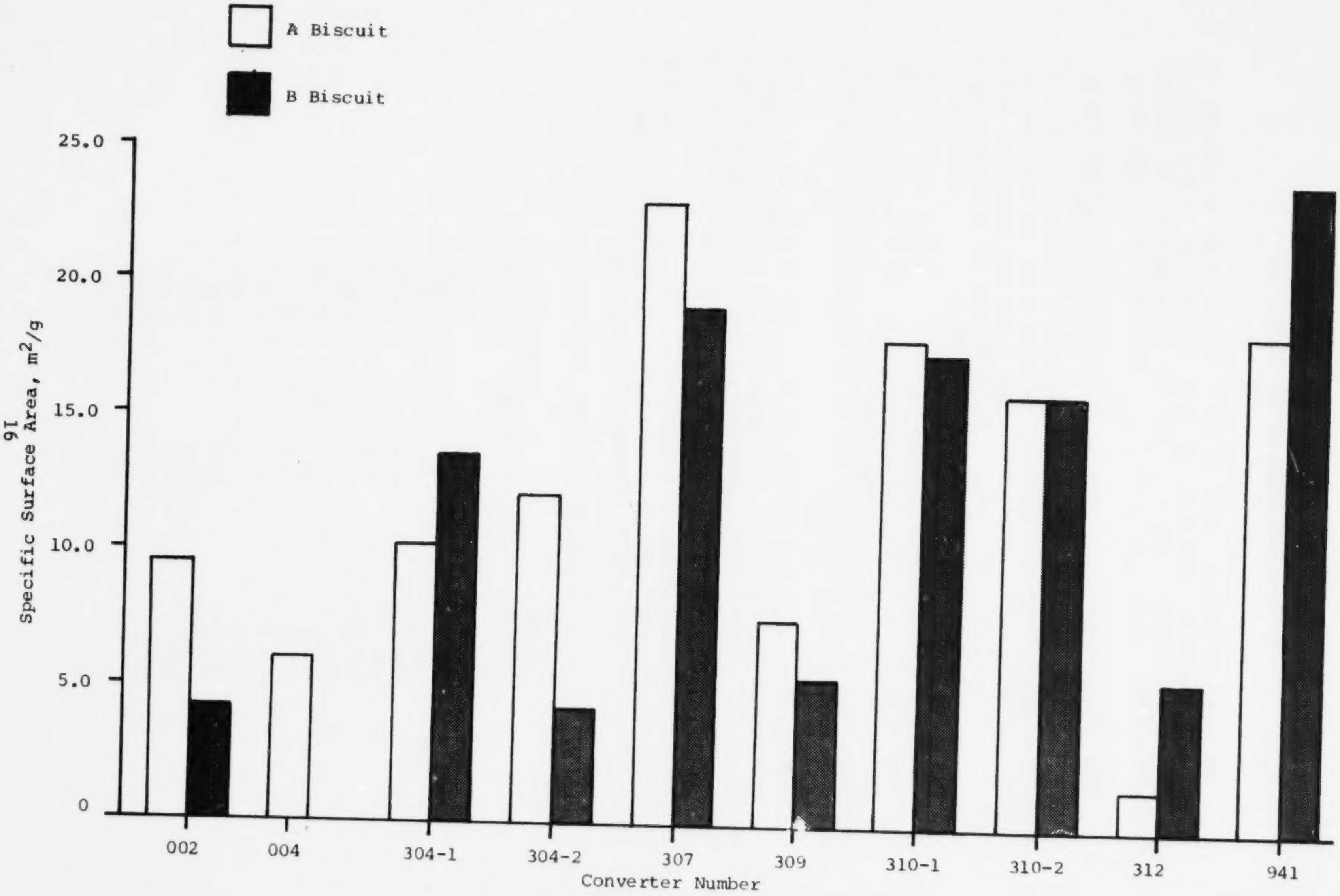

Figure 6. Specific surface areas of misfueled converters

VI. ELEMENTAL ANALYSIS BY X-RAY FLUORESCENCE

One half of each biscuit was ground into a homogeneous sample for analysis by x-ray fluorescence. The procedures used to take and analyze the samples are given in Appendix A. The elements of concern included phosphorus (P), sulfur (S), calcium (Ca), manganese (Mn), zinc (Zn), lead (Pb), platinum (Pt), palladium (Pd), and rhodium (Rh). Nickel (Ni) was added to the list when high concentrations were observed. The elements P, S, Ca, Mn, Zn and Pb are present in the converters as poisons and contaminants. These elements are derived from engine wear, dirt deposits, oil, fuel, etc. The noble metals (Pt, Pd, and Rh) are the catalyst metals which perform the function of "cleaning up" the exhaust. Nickel is also a metal which exhances the catalytic activity. One example which has been observed is the decrease in ammonia formation due to the addition of nickel to the catalyst.(3,4) Aluminum and silicon are major constituents of the substrate but were not quantitatively determined.

The weight percent of each element was determined by the analytical procedure. The results of the analyses are presented in Table 6. The levels for Mn and Rh in the samples were below the detection limits of the procedure. Figures 7 through 11 illustrate the weight percent values for S, Pb, Ni, Pt, and Pd. In general, the S concentration was higher on the second biscuit, while the Ni and Pb concentrations were greater on the first. The exceptions included the Chrysler converter (309), which had a higher weight percent of Pb on the second biscuit, and converter 941, which had a higher weight percent S on the first biscuit. Platinum and palladium were found in all of the biscuits except the Chrysler (309), which had only Pt in biscuit A and only Pd in biscuit B. The Chrysler converter (309) and the VW converter (004) did not contain any Ni. The weight of each element in the biscuit can be determined by multiplying the weight percent by the weight of each biscuit and dividing by 100. These values are presented in Table 7, which shows the weight of each element in each individual biscuit.

Table 8 shows a comparison of the noble metals and Ni by the vehicle makes. Each manufacturer used about the same amount of nickel in the various catalysts, but the Pt/Pd/Rh ratios are different for each vehicle.(5) This difference is probably related to the engine size and type of emission control for each particular vehicle. The ratios of Pt to Pd in the misfueled converters were very much different from those reported by the manufacturer. The reason for this difference is not known. The minimum detection limit for Rh is 0.01 weight percent. Since Rh is added to converters in concentrations at or below the detection limit, it becomes difficult to determine the sample concentrations. The presence of large amounts of Pb attenuates the fluoresced x-rays which also interferes with the detection of Rh.

TABLE 6. ELEMENTAL ANALYSIS OF NOBLE METALS AND POISONS IN INTENTIONALLY LEADED CATALYSTS

Biscuit Number	Elements, wt. %									
	P	S	Ca	Mn	Ni	Zn	Pb	Pt	Pd	Rh
002-A	0.07	0.24	0.01	*[a]	1.84	trace[b]	3.17	0.08	0.04	*
002-B	*	1.81	0.01	*	0.08	*	2.24	0.14	0.19	*
004	0.22	1.46	0.03	*	*	0.03	2.29	0.15	0.07	*
304-1-A	0.18	0.82	0.02	*	2.00	0.02	2.28	0.16	trace	*
304-1-B	0.04	1.14	0.02	*	0.10	trace	1.33	0.15	0.28	*
304-2-A	0.28	0.65	0.02	*	2.10	0.03	2.78	0.14	trace	*
304-2-B	trace	1.13	0.02	*	0.10	trace	1.33	0.13	0.24	*
307-A	*	1.00	*	*	1.80	*	1.70	0.14	0.09	*
307-B	*	1.55	trace	*	trace	*	1.47	0.18	0.13	*
309-A	*	0.79	0.02	*	*	*	0.68	0.15	*	*
309-B	*	1.22	0.02	*	trace	*	2.32	*	0.64	*
310-1-A	0.05	0.82	0.02	*	2.41	trace	2.15	0.39	0.28	*
310-1-B	*	1.36	0.02	*	0.31	*	1.00	0.17	0.08	*
310-2-A	trace	0.86	0.02	*	2.22	trace	2.04	0.34	0.33	*
310-2-B	*	1.05	0.02	*	0.26	*	0.75	0.15	0.20	*
312-A	*	0.50	0.02	*	1.88	trace	1.30	trace	0.20	*
312-B	trace	0.82	0.01	*	0.03	trace	0.69	0.30	0.20	*
941-A	*	1.19	*	*	1.45	*	1.82	0.10	0.08	*
941-B	*	0.85	trace	*	*	*	0.53	0.18	0.24	*
detection limit	0.03	0.03	0.007	0.005	0.01	0.01	0.01	0.02	0.02	0.01

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[a] *Element concentration below detection limit

[b] Element concentration at detection limit

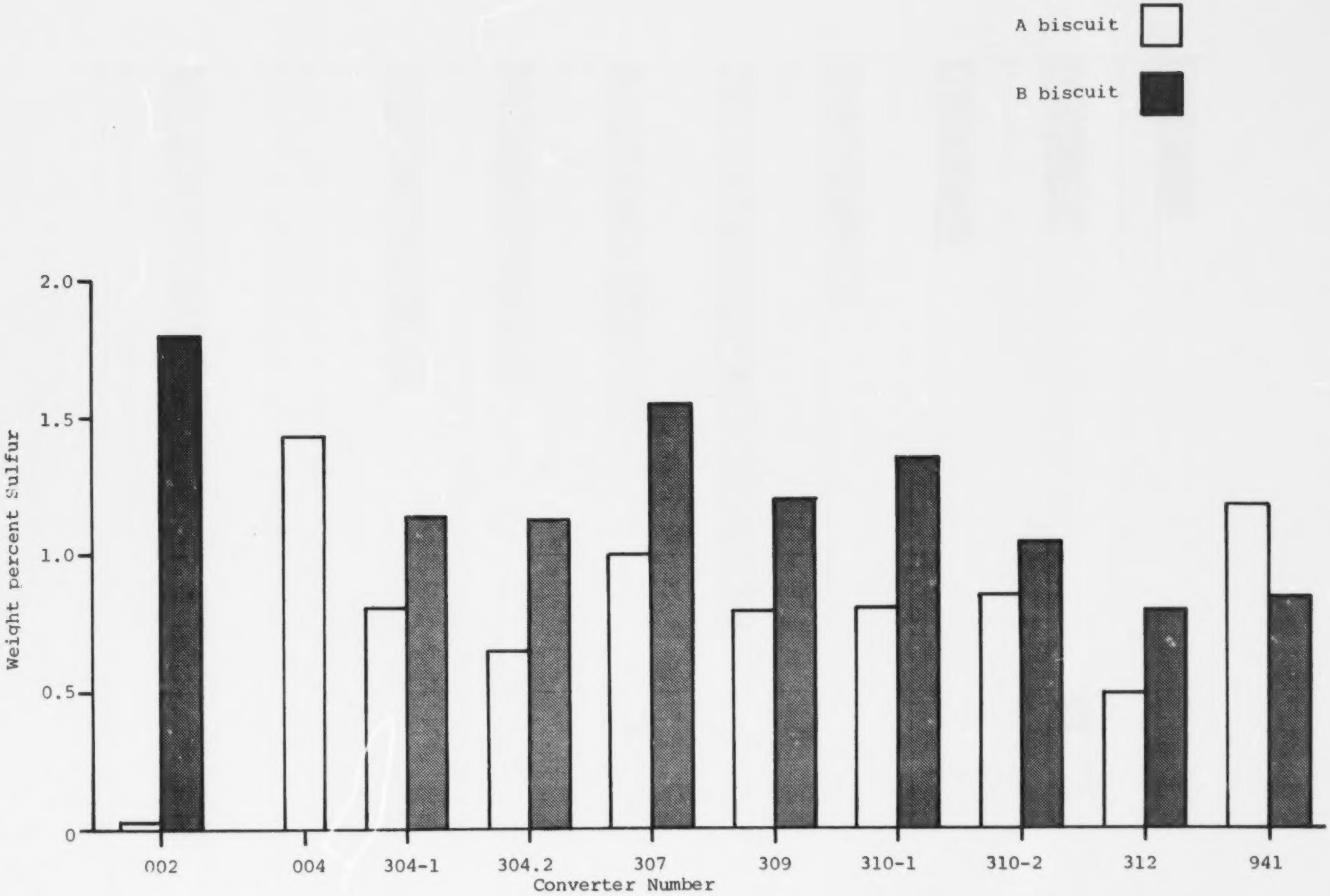

Figure 7. Weight percent sulfur

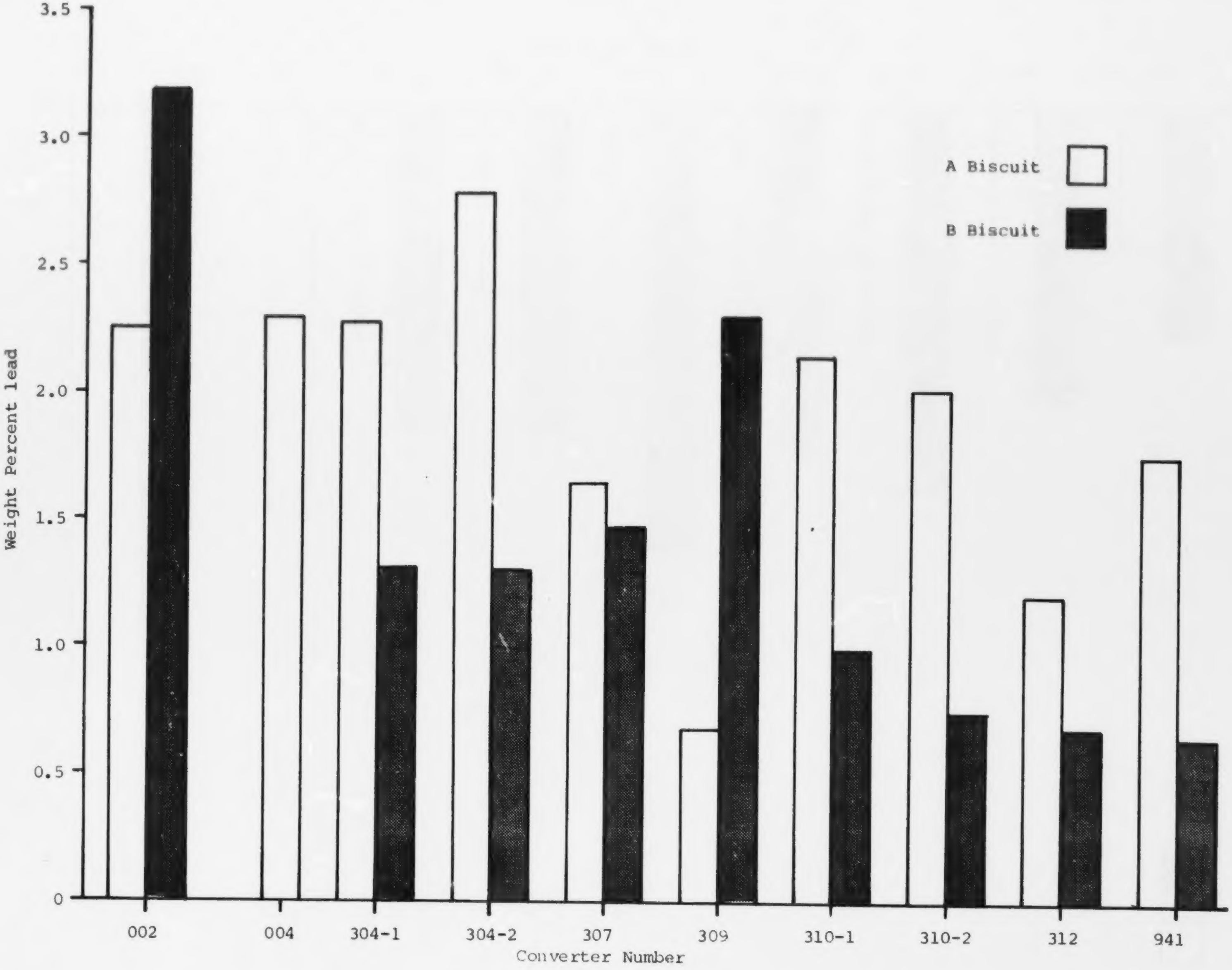

Figure 8. Weight percent lead

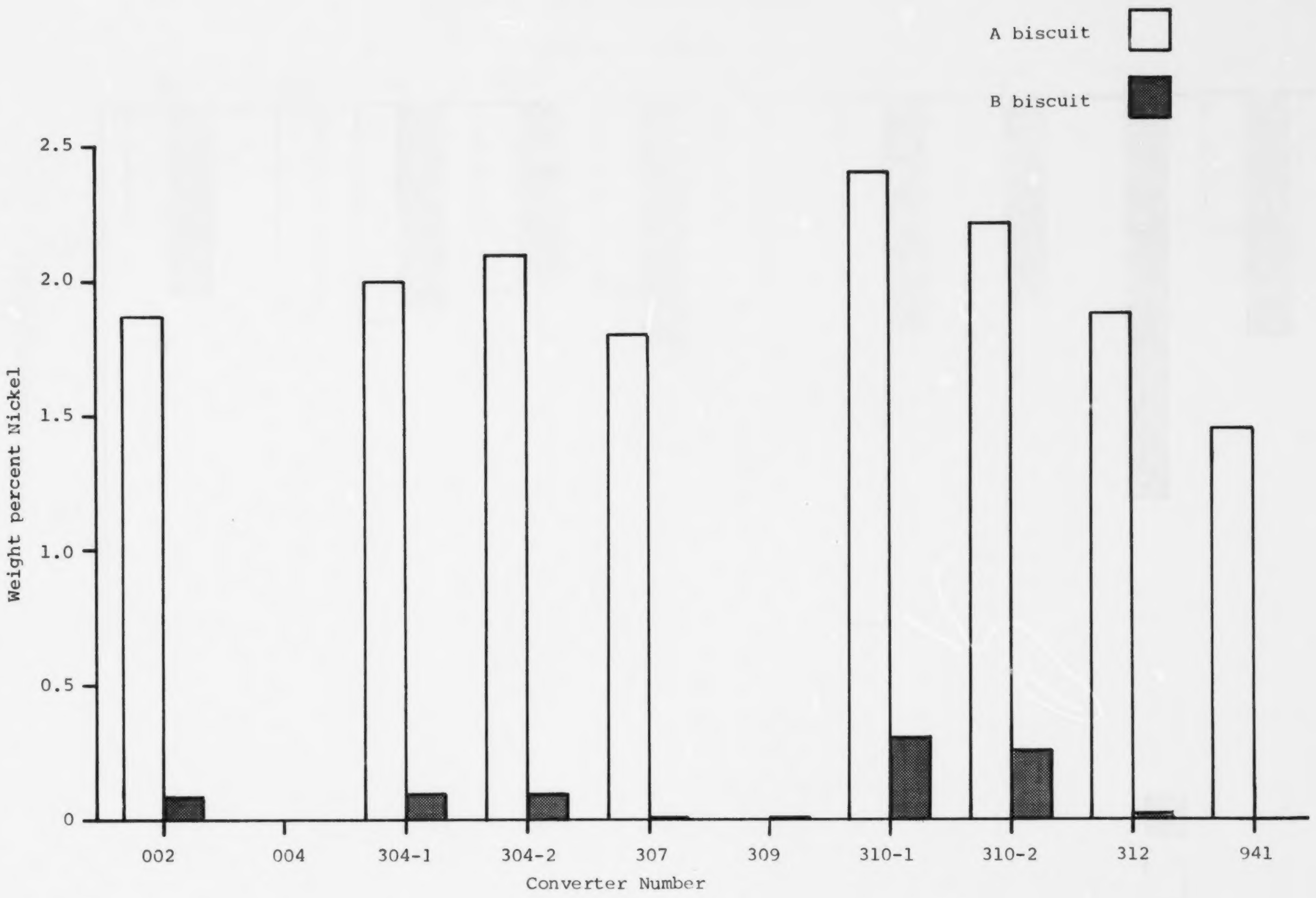

Figure 9. Weight percent nickel

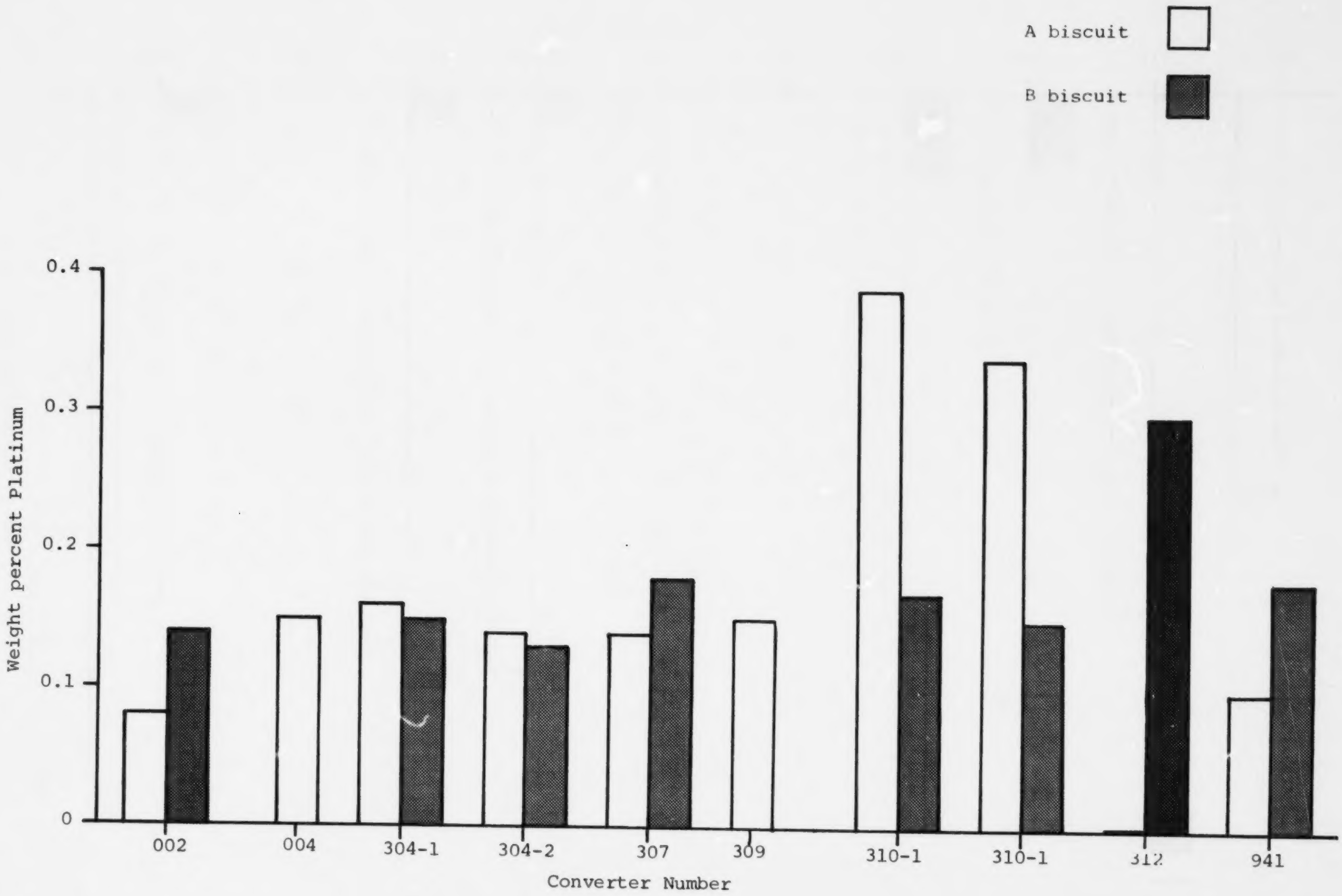

Figure 10. Weight percent platinum

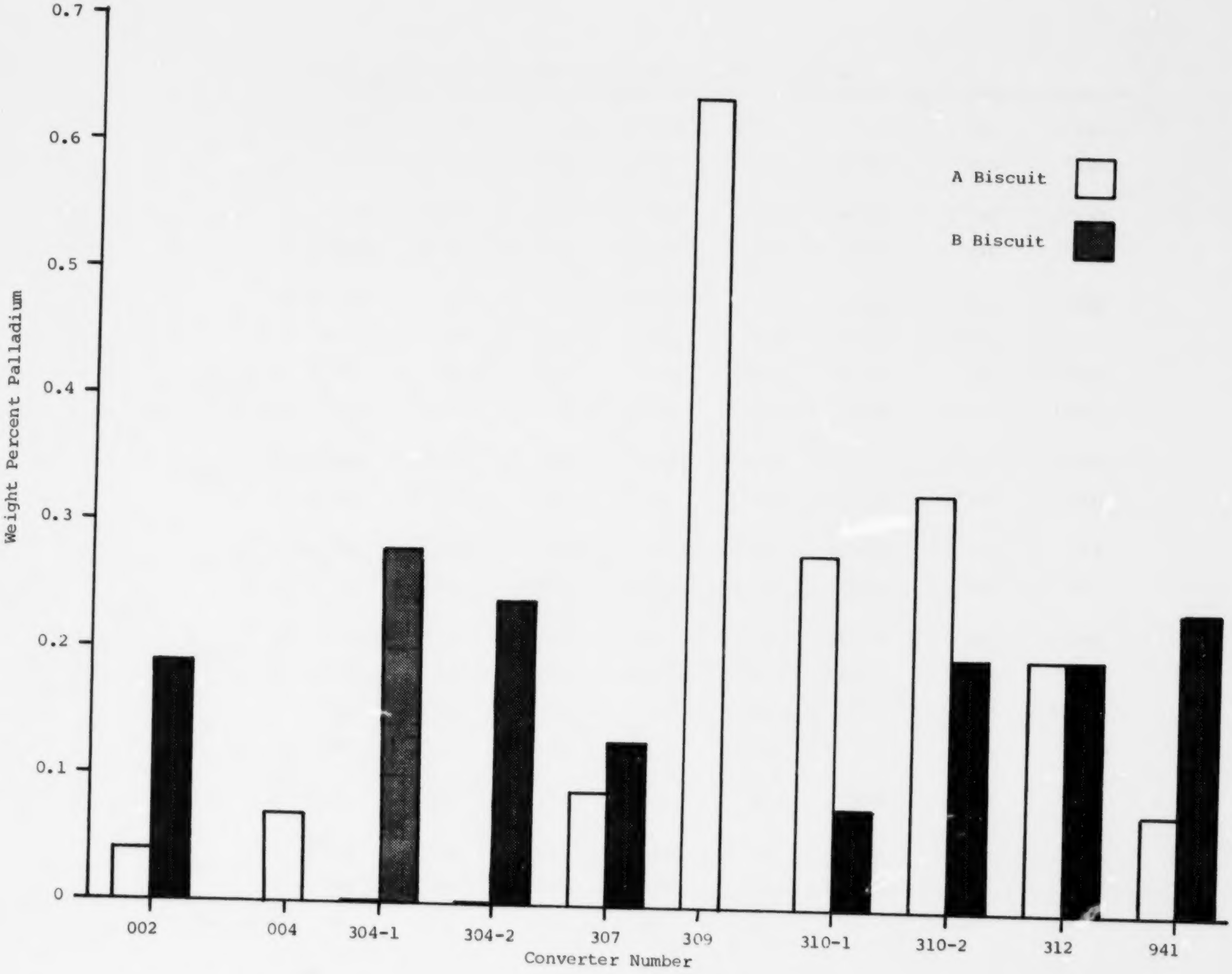

Figure 11. Weight percent palladium

TABLE 7. MASS IN GRAMS OF METALS AND POISONS IN INTENTIONALLY LEADED CONVERTERS

CONVERTER ID		P	S	CA	NI	ZN	PB	PT	PD
002	A	.282	.966	.040	7.408	.040*	12.762	.322	.161
	B	0.000	6.748	.037	.298	0.000	8.351	.522	.708
004	A	2.061	13.674	.281	0.000	.281	21.448	1.405	.656
304-1	A	.888	4.043	.099	9.862	.099	11.243	.789	.099*
	B	.178	5.062	.089	.444	.044*	5.905	.666	1.243
304-2	A	1.319	3.062	.094	9.891	.141	13.094	.659	.094*
	B	.135*	5.096	.090	.451	.045*	5.998	.586	1.082
307	A	0.000	8.942	0.000	16.096	0.000	15.201	1.252	.805
	B	0.000	11.245	.051*	.073*	0.000	10.665	1.306	.943
309	A	0.000	8.774	.222	0.000	0.000	7.552	1.666	0.000
	B	0.000	5.822	.095	.048*	0.000	11.071	0.000	3.054
310-1	A	.195	3.205	.078	9.421	.039*	8.404	1.525	1.095
	B	0.000	6.146	.090	1.401	0.000	4.519	.768	.362
310-2	A	.118*	3.383	.079	8.733	.039*	8.025	1.338	1.298
	B	0.000	4.318	.082	1.069	0.000	3.084	.617	.822
312	A	0.000	4.157	.166	15.628	.083*	10.807	.166	1.663
	B	.215*	5.864	.072	.215	.072*	4.934	2.145	1.430
941	A	0.000	11.247	0.000	13.704	0.000	17.201	.945	.756
	B	0.000	6.172	.051*	0.000	0.000	3.848	1.307	1.743

* TRACE QUANTITY CALCULATED FROM MINIMUM DETECTION LIMIT

TABLE 8. COMPARISON OF NOBLE METALS BY MANUFACTURER

			Concentration, g/biscuit			Manufacturers		
				Noble Metals*		Noble Metal Ratios		
Converter	Biscuit	Make	Ni	Pt	Pd	Pt	Pd	Rh
002		Ford	7.41	0.32	0.16	5		1
			0.30	0.52	0.71	5	2	
304-1		Ford	9.86	0.79	0.10	5		1
			0.44	0.67	1.24	3	2	
304-2		Ford	9.89	0.66	0.09	5		1
			0.45	0.59	1.08	3	2	
310-1		Ford	9.42	1.53	1.10	12.2		1
			1.40	0.77	0.36	3	2	
310-2			8.73	1.34	1.30	12.2		1
			1.07	0.62	0.82	3	2	
307		GM	16.10	1.25	0.81	5	2	1
			0.07	1.31	0.94	7	1	
312		GM	15.63	0.17	1.66	3	3	1
			0.22	2.15	1.43	8	1	
941		GM	13.70	0.95	0.76	5	2	1
			0.00	1.31	1.74	5	2	
309		Chrysler	0.00	1.67	0.00	10		1
			0.05	0.00	3.05		Pd only	
004		VW	0.00	1.41	0.66	5		1

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*Rh concentration below the detection limit for the analytical procedure

Several other elements were determined qualitatively. Cerium (Ce), titanium (Ti), and iron (Fe) were found in all of the converters. The exceptions to this were the B biscuits from the GM converters (307, 312, and 941), which did not contain Ce, and the B biscuit of the Chrysler converter (309), which did not contain Ce or Ti. Titanium was probably present in the converters as a whitening agent (an agent to enhance the aesthetic appearance of the ceramic substrate)(6) or as an impurity of the cordierite substrate, and Ce was added to inhibit the conversion of gamma-alumina (higher surface area) to alpha-alumina (lower surface area) at the elevated temperatures experienced within the converter.(7) The Fe was present from the engine and exhaust system (i.e., rust and engine wear products).

VII. SCANNING ELECTRON MICROSCOPE

The surfaces of each biscuit were examined with the use of a scanning electron microscope (SEM). A one cubic-centimeter piece was taken from the front face of each biscuit. The internal surfaces of the individual cells from each biscuit were examined for indications of lead deposits and other indications of changes to the catalyst surfaces. Photographs of a typical surface were taken and are included in Appendix E. All examinations and photographs were taken at a magnification of X500. This magnification was selected because the interesting structures could be examined without severely limiting the field of view.

A typical example of what is probably a lead deposit on the surface is shown in Figure 12. The deposits covering the surface of the catalyst have the appearance of very fine grains spread evenly over the surface. Very few large pores were observed. The physical structures for all of the A biscuits were quite similar in appearance. The appearances of the surface for the B biscuits were also similar, but different from the A biscuits. These had the appearance of dried, cracked mud with the exception of two of the GM converters (307 and 941), which were unique in surface structure, and the Chrysler converter (309), which was the converter with the highest lead concentration on the B biscuit. Converter 307 also had a high lead and sulfur content on the B biscuit (10.67 g lead or 1.47 weight percent and 11.25 g sulfur or 1.55 weight percent). The physical appearance of the B biscuit from the Ford converter (002) was very similar to the A biscuits (fine grains), except that a number of cracks were still visible. Some of the cracks appeared to be partially filled with the same material that covered the surface. For dual catalyst vehicles, the physical appearances of the individual biscuits were quite similar. The surface appeared very smooth, with deep cracks and a number of large, randomly-dispersed particles of unknown composition on the surface.

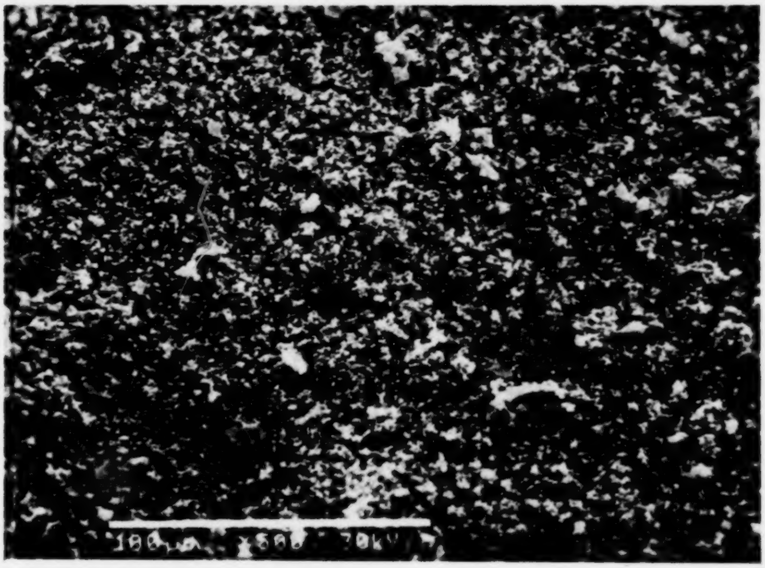

Figure 12. Typical example of catalyst surface from misfueled vehicle (GM-vehicle 307)

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VIII. ANALYSIS OF TEST RESULTS

The results of the analytical procedures performed on the ten catalysts evaluated during this project are most useful if they can be correlated with changes in emission levels of the vehicles on which the catalysts were installed. These catalysts were from vehicles involved in several different EPA studies, and represented only a portion of the vehicles involved in each study. While the catalysts did come from different studies, the studies all involved the intentional use of leaded fuel in a catalyst vehicle. EPA furnished SwRI with the vehicle emission test results and amount of fuel lead that was used in each vehicle.

There are two types of statistical analysis that can be done on the analytical procedure results from this study. One is a correlation study among the results from the various analytical procedures. The second analysis is a correlation between the analytical procedure results and both the fuel lead used and the changes in vehicle emission levels.

Correlation Matrix of Analytical Procedure Results

As an initial step to determine if any correlation exists between the levels of the various elements found on the catalyst, a correlation matrix of pairwise regressions was obtained using the BMDP statistical computer program. Included in the matrix were the values for each catalyst of percent by weight of eight of the elements from the XRF analysis, plus the specific surface area in m^2/g from the BET analysis. This matrix is shown in Table 9. In the matrix, a value of 1.0 indicates a perfect linear relationship. A negative value indicates an inverse relationship. The highest value in the matrix is for the zinc and phosphorus correlation. This is not surprising since a zinc and phosphorus compound, zinc dialkyldithiophosphate, is an engine oil additive. The zinc and calcium correlation, while much lower than the zinc-phosphorus correlation, is also the result of both zinc and calcium being included in engine oil additives.

The second highest correlation coefficient is for nickel and sulfur. This coefficient is negative, indicating that as nickel increased the sulfur level decreases. The reason for this correlation is not immediately evident. As was pointed out in a previous section of this report, nickel was found in the first biscuit of each two-biscuit catalyst, except the catalyst from vehicle 309. The amount of nickel in these first biscuits, on the order of two percent by weight, is too large to be a result of engine wear. Since these systems were all three-way (oxidation and reduction) catalysts, the nickel is presumed to be included in the first biscuit as a reduction catalyst. The highest sulfur levels were in the second biscuit, except for the catalyst from vehicle 941. In a previous SwRI study of oxidation catalysts conducted for EPA,(8) sulfur levels were generally higher in the first biscuit. Thus, while the sulfur level being higher in the second biscuit appears to be a characteristic of three-way catalyst systems with an oxidation catalyst as the second biscuit, it is difficult to ascribe a cause-and-effect relationship to the correlation of nickel and sulfur levels. It is interesting that there is only a slight negative correlation between lead and surface area (labeled SSA in Table 9). One of the ways lead has been

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TABLE 9. CORRELATION AMONG ELEMENTS FOUND ON CATALYSTS

		P 1	S 2	CA 3	NI 4	ZN 5	PB 6	PT 7	PD 8	SSA 9
P	1	1.0000								
S	2	-.1842	1.0000							
CA	3	.4507	-.0355	1.0000						
NI	4	.3137	-.5919	-.0677	1.0000					
ZN	5	.9380	-.2607	.5548	.3372	1.0000				
PB	6	.5601	-.1186	.0896	.5457	.4975	1.0000			
PT	7	.0344	-.0215	.0522	.2094	.1053	-.1408	1.0000		
PD	8	-.3859	.1642	.1507	-.2024	-.2830	-.0367	-.0091	1.0000	
SSA	9	-.1756	.0401	-.4760	.1952	-.3241	-.1787	.3604	-.1234	1.0000

hypothesized to poison catalysts is by reducing the surface area. No good examples were available from this group of converters where lead poisoned the catalyst without changing the surface area.

There are only two other correlation coefficients above 0.50. These correlations are between lead and phosphorus and lead and nickel. Again, the reason for these correlations is not obvious. These relationships may warrant further study, but such investigation is beyond the scope of this project.

Correlation Matrix for Analytical Results from the Catalysts and Vehicle Emissions

The EPA has furnished the results of the emission tests on the vehicles from which the catalysts in this project were taken. The emission test results were for FTP tests both before using leaded fuel and at the end of the vehicle operation on leaded fuel. The percent change in each of the FTP emissions was calculated. These values are shown in Table 10. The emission changes could have been expressed in grams/mile. However, percent change was chosen in an attempt to normalize the data, because of the large differences in the initial CO emissions between cars (see Table 2). Since the emission results are for a vehicle, if correlations to catalyst condition are desired, the various catalyst parameters must be recalculated in terms of a single number for all biscuits and catalysts associated with each vehicle. These recalculated values represent an overall average level for the engine-catalyst system, and are shown in Table 11.

The overall catalyst parameters and the emission changes as well as the amount of fuel lead put through each vehicle were used to generate another correlation matrix. This matrix is shown in Table 12. As would be expected, the highest correlation coefficient is for the lead retained in the catalyst and the fuel lead put through vehicle, labeled GPB in Table 12. Thus, any other variable that correlates well with one of these parameters will correlate well with the other also. This can be seen in correlations between fuel lead and phosphorus and between fuel lead and zinc. It is hypothesized that these correlations are the result of the fuel lead scavengers also scavenging the zinc additive from the oil, with subsequent deposition of the zinc and phosphorus on the catalyst.

The correlation between zinc and phosphorus has been explained above. The negative correlation between surface area and zinc and calcium, and to a lesser extent, phosphorus and lead, probably results from some plugging of the catalyst surface by these elements.

Elements such as platinum, palladium, and nickel which are part of the catalyst when new, would decrease in weight percent as a catalyst increased in weight due to deposits, particularly lead. The lead retained on the catalysts examined increased catalyst weight approximately one to three percent. Thus, for any element whose weight did not change over the test period, there would be a negative correlation with lead. There is a strong negative correlation between palladium and lead, and a much lower negative correlation between platinum and lead. Nickel shows a slight negative correlation only with lead

TABLE 10. PERCENT CHANGE IN EMISSIONS FOR EIGHT VEHICLES OPERATED ON LEADED FUEL

Vehicle No.	Study No.	Percent Change After Operation on Leaded Fuel HC	CO	NO_x
002	ATL #1	275.4	235.6	39.0
004	ATL #1	324.2	11.4	102.0
304	ATL #5	385.3	164.4	-2.3
307	ATL #5	540.9	97.0	68.4
309	ATL #6	222.5	43.7	-17.0
310	ATL #6	262.2	17.2	69.1
312	ATL #6	77.5	10.3	46.3
941	EPA In-House	241.2	95.8	8.7

TABLE 11. AVERAGE XRF AND BET ANALYSIS RESULTS FOR CATALYST SYSTEMS ON EIGHT CARS

Car No.	Total Wt. of Cat. Material,g	Percent by Weight P	S	Ca	Ni	Zn	Pb	Pt	Pd	Specific Surface Area m^2/g
002	775.4	0.04	1.00	0.01	1.00	0.04	2.70	0.11	0.10	7.10
004	936.6	0.22	1.50	0.03	0.00	0.03	2.30	0.15	0.07	6.00
304	1859.1	0.14	0.90	0.02	1.10	0.02	1.90	0.14	0.13	10.26
307	1619.7	0.00	1.20	0.00	1.00	0.00	1.60	0.16	0.11	21.24
309	1587.8	0.00	0.90	0.02	0.00	0.00	1.20	0.10	0.19	7.01
310	1647.4	0.02	1.00	0.02	1.30	0.01	1.50	0.26	0.20	16.98
312	1546.4	0.04	0.60	0.10	1.00	0.01	1.00	0.15	0.20	3.35
941	1671.2	0.00	1.00	0.00	0.80	0.00	1.30	0.14	0.10	20.83

TABLE 12. CORRELATION BETWEEN CATALYST ELEMENTS AND EMISSION CHANGES

		P 1	S 2	CA 3	NI 4	ZN 5	PB 6	PT 7	PD 8	SSA 9	HC 10
P	1	1.0000									
S	2	.5167	1.0000								
CA	3	.1398	-.5426	1.0000							
NI	4	-.3557	-.4306	.0320	1.0000						
ZN	5	.5947	.2817	.0187	-.0620	1.0000					
PB	6	.5214	.5635	-.4066	-.0416	.8904	1.0000				
PT	7	-.0429	.0896	.0359	.5097	-.2662	-.1823	1.0000			
PD	8	-.4655	-.7333	.5120	.2257	-.4921	-.6874	.3370	1.0000		
SSA	9	-.4548	.2360	-.6335	.3986	-.5638	-.2021	.4244	-.1854	1.0000	
HC	10	.1383	.6140	-.6748	.0987	-.0165	.3812	.0643	-.5366	.5461	1.0000
CO	11	-.0894	-.0559	-.4857	.3494	.4945	.6148	-.4402	-.4430	.0706	.3375
NOX	12	.3968	.6001	.1359	.0303	.3047	.3377	.5158	-.2866	.0324	.2216
GPB	13	.6566	.3961	-.2188	.0528	.8660	.9121	-.2364	-.6127	-.3138	.4145

		CO 11	NOX 12	GPB 13
CO	11	1.0000		
NOX	12	-.3518	1.0000	
GPB	13	.6342	.2277	1.0000

retained in the catalyst, but not fuel lead. However, it is known that not all catalysts contained the same weight percent of nickel, a prerequisite for a correlation of this kind. If it is assumed that all catalysts started with the same weight percent of palladium, but not the same weight percent of platinum, then catalyst weight gain could explain the high negative correlation between lead and palladium.

There are other correlations that might warrant further study: sulfur correlates reasonably well with phosphorus, calcium, and palladium. Calcium and palladium, as well as nickel and platinum correlate moderately well. However, investigation of these relationships is beyond the scope of this project.

A discussion of the correlation of emission changes has purposely been left until last. All vehicle emissions increased after being operated on leaded fuel, except for NO_x from vehicles 304 and 309. Thus, it would be reasonable to expect good correlations between emissions and lead. Only CO shows even a moderate correlation with lead. NO_x and HC both correlate best with sulfur. HC also has a moderate negative correlation with calcium and palladium. The moderate positive correlation between HC and surface area is puzzling since emissions would be expected to increase as surface area decreased. It must be kept in mind that the emission values used were percent changes from baseline. Of all the elements quantified, only lead could be presumed to be zero at the baseline test. Therefore, correlations with elements other than lead may have little meaning. Also, the correlation matrix is for linear relationships. Non-linear relationships may not show high linear correlation coefficients. For this reason, the relationships between change in emissions and lead retained on the catalyst were examined in greater detail.

Effect of Catalyst Lead Levels on Vehicle Emissions

As mentioned above, all emissions on all vehicles increased after being driven using leaded fuel, except for NO_x emissions from vehicles 304 and 309. The average percent increases were 291 percent for HC, 84 percent for CO, and 39 percent for NO_x. The minimum, maximum, mean, standard deviation and coefficient of variation of the percent changes in emissions are listed in Table 13.

TABLE 13. SUMMARY STATISTICS FOR EMISSION CHANGES FOR EIGHT CARS OPERATED ON LEADED FUEL

	Percent Change in Emission				Coefficient
Emission	Minimum	Maximum	Mean	S.D.	of Variation
HC	77.5	540.9	291.1	134.3	46.1%
CO	10.3	235.6	84.4	81.5	96.6%
NO_x	-17.0	102.0	39.3	40.6	103.3%

Since the eight vehicles whose emissions are included in Table 10 represent only a part of the vehicles used in the leaded fuel projects, the means given in Table 13 should be compared with the means from all the vehicles to ensure that this subgroup is representative of the entire group of vehicles. The emission results from all of the vehicles in the leaded fuel studies are not available to SwRI at this time.

The large coefficient of variation indicates that the percent change in emissions is a function of one or more parameters that vary from vehicle to vehicle. An obvious parameter is the amount of lead retained in the catalyst. To prevent the differences in catalyst size from confusing the results, retained lead was expressed in terms of percent by weight for the total catalyst system. The correlation matrix had shown that only CO demonstrated even a moderate linear correlation with weight percent of lead. Plots of the percent changes in emissions as a function of weight percent of lead retained in each catalyst are shown in Figures 13, 14, and 15 for HC, CO, and NO_x, respectively. It is difficult to see any trends, either linear or non-linear, in these plots. The changes in emissions must therefore result from a number of other factors along with retained lead.

The catalysts examined were from eight cars, representing four different manufacturers and eight different engines. It is possible that each engine and catalyst combination has its own relationship between catalyst lead and emissions. If more catalysts were examined so that there would be a number of data points for each engine, an analysis of variance could be performed to determine if the change in emissions was a function of engine model. Unfortunately, the current data set is not sufficient for an analysis of variance. Thus, it is not possible from the information available at SwRI to determine the reason for the large variation in emissions changes.

Catalyst Lead as a Function of Fueling Schedule

There were four different schemes used to put leaded fuel into the vehicles whose catalysts were evaluated during this project. It was hoped that the results of the catalyst analyses could be used to show what effect, if any, the fueling scheme had on the amount of lead retained in the catalyst. If it is assumed that the catalysts were all sized similarly for the engines on which they were installed, and that engine thermal efficiency is close to the same value for all engines, then the rate at which the lead was passed through a catalyst, in terms of grams/minute per cubic foot of catalyst, should be approximately the same for all vehicles. To alleviate the need to assume that the catalysts were sized similarly, the grams of fuel lead were divided by the weight in grams of each catalyst. For vehicles 304 and 310, which were dual catalyst vehicles, one half of the total lead used in the vehicle was assumed to pass through each catalyst. This variable, grams of fuel lead per gram of catalyst on a per catalyst basis, is a variation of the variable, grams of fuel lead per gram of catalyst on a per vehicle basis, that was used in the correlation matrix, and showed a high correlation between fuel lead and lead retained. The relationship between fuel lead and lead retained on a per catalyst basis is plotted as Figure 16. The different leaded fuel fueling schemes are shown in the figure by different symbols. Note that the values of the fuel lead parameter for each fueling scheme tend to cluster together at different levels. None of the values from the every-fourth-tankful fueling scheme have values as high as the every-tankful or every-other-tankful fueling scheme.

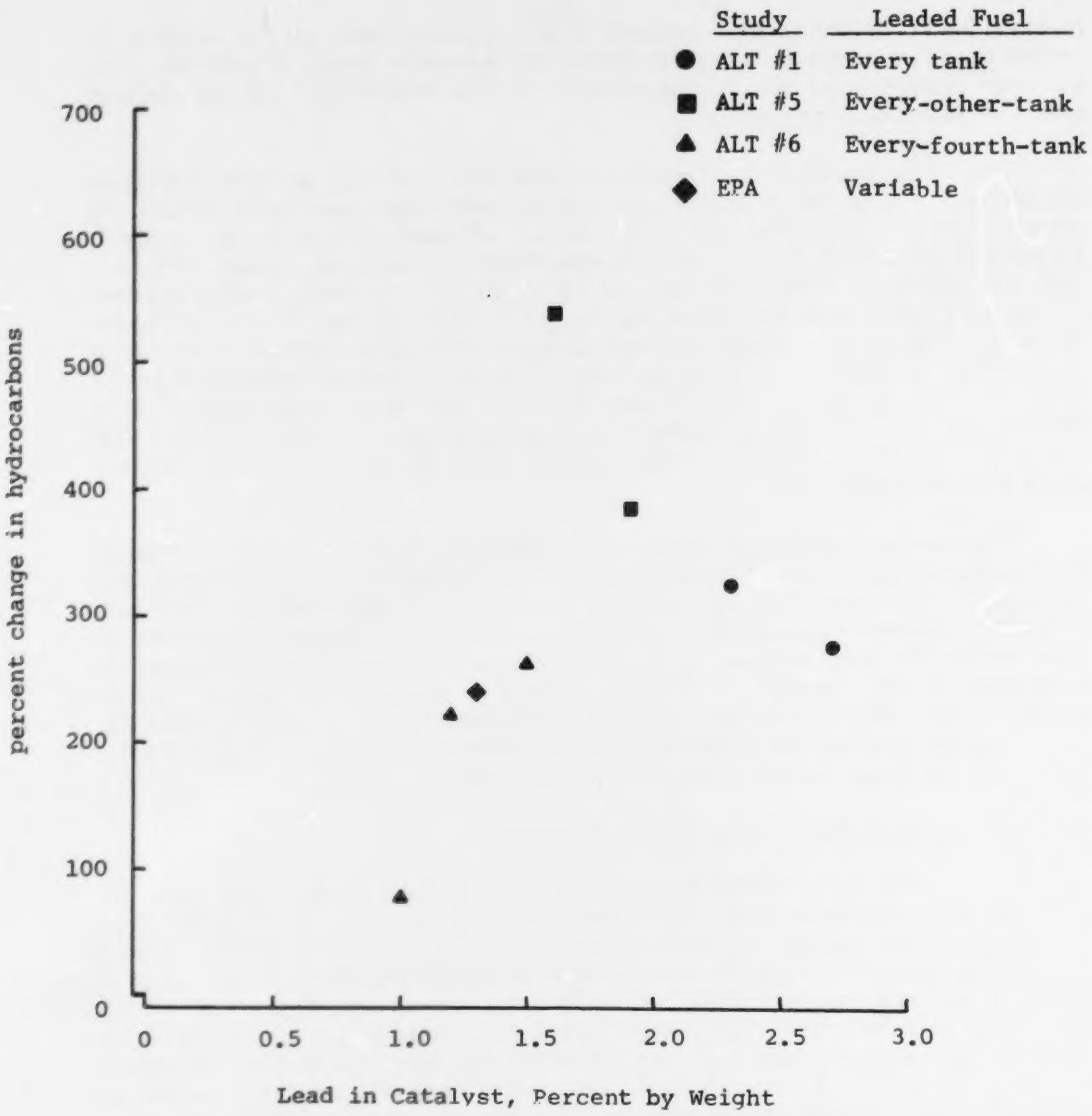

Figure 13. Percent change in Hydrocarbons

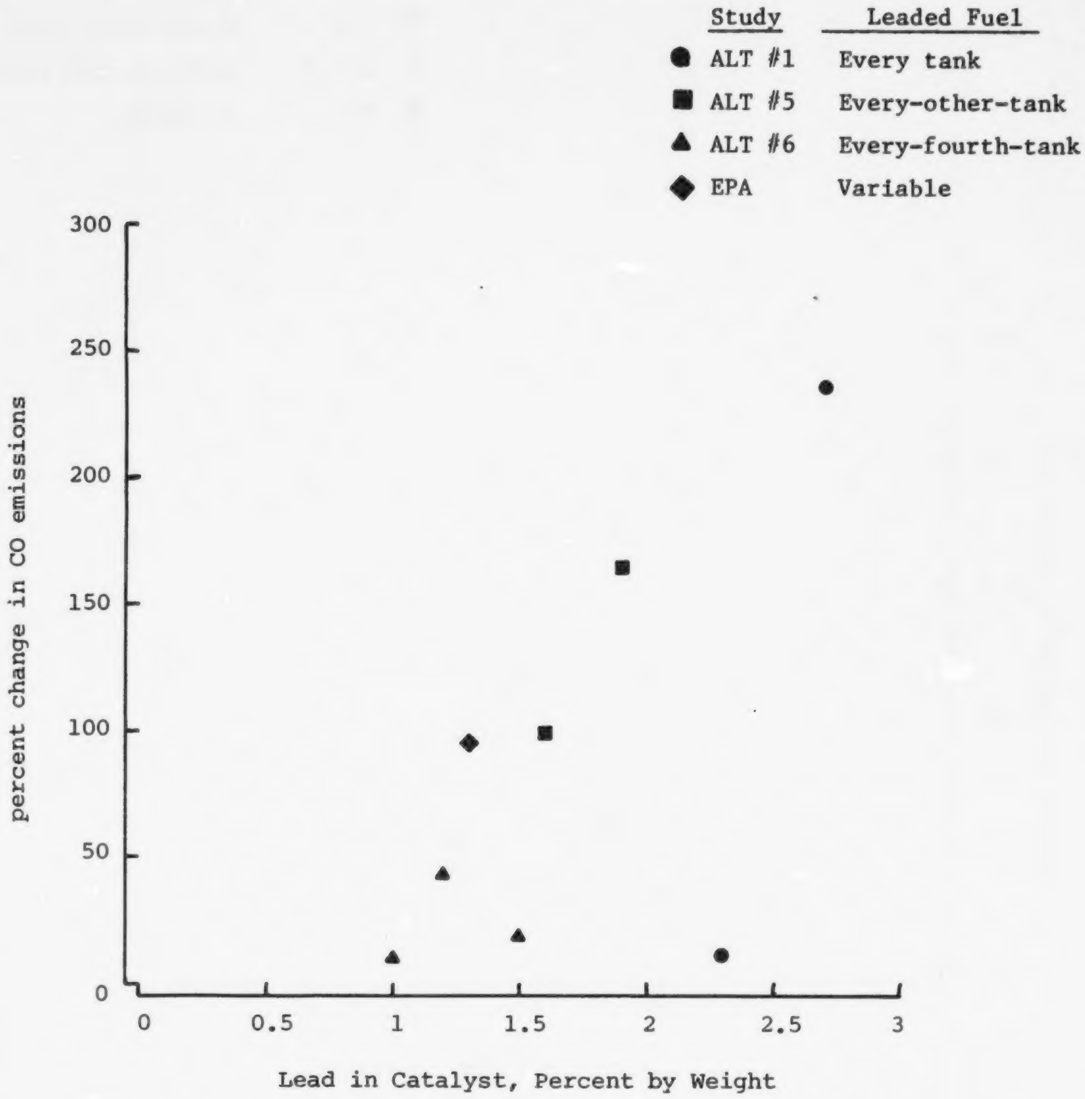

Figure 14. Percent change in CO emissions

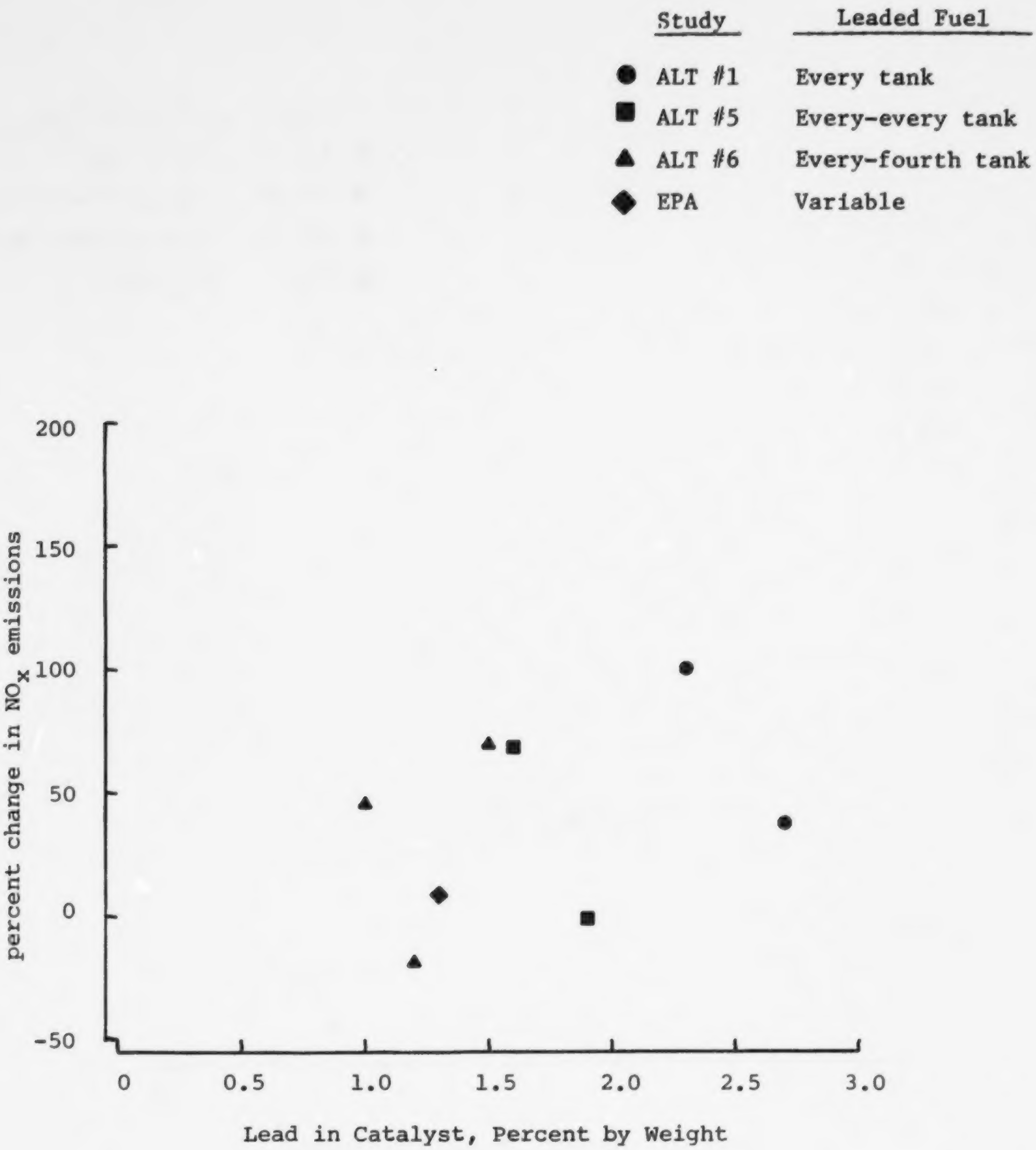

Figure 15. Percent change in NO_x emissions

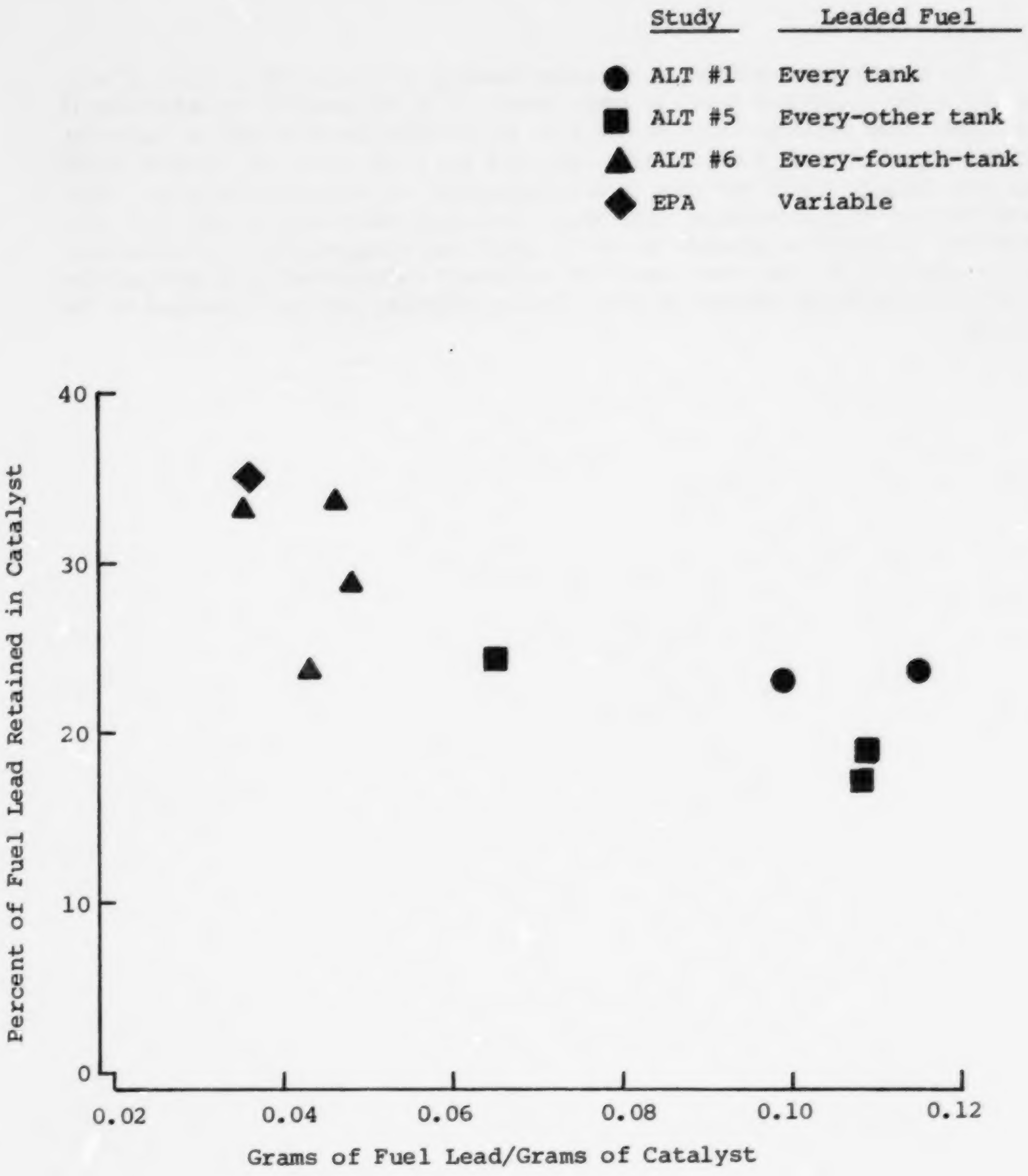

Figure 16. Percent of fuel lead consumed/grams of catalyst

Thus, it is not possible to separate fueling scheme effects from effects caused by the amount of lead. In other words, it is not possible to determine if the higher lead retention seen in the ATL #6 vehicles for example, is caused by the fueling scheme or the fact that less lead (on a per gram of catalyst basis) was put through these vehicles, or a combination of these two factors. Since there are additional vehicles that were operated under the leaded fuel test programs, it might be possible to select additional catalysts for evaluation in a future program, so that there would be sufficient data spread to determine the relationship between amount of lead, fueling scheme, and lead retained in the catalyst.

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APPENDIX A

SAMPLING AND ANALYSIS PROCEDURES

A. Radiograph of Whole Monolith Converters

B. Disassembly of Whole Converters

C. Sample Preparation and Distribution

D. Surface Area by BET Analysis

E. Elemental Analysis by X-Ray Fluorescence

F. Examination by Scanning Electron Microscope

G. Photographs of Converter Bisquits

SAMPLING AND ANALYSIS PROCEDURES

For this project, the catalytic converters to be examined were received completely intact, i.e., as removed from an automobile. The catalysts had to be removed from the protective housing before the samples could be taken. The methods used to remove the catalytic material from the converter container and to divide the material into samples for analysis are explained in this section.

A. Radiograph of Whole Monolith Converters

From previous work, SwRI had found that radiographs (x-rays) of whole monolith converters could identify cracks, substrate meltdown, blowout and other structural failures, prior to disassembling the converter. This knowledge is needed to prevent inadvertent disturbance of these problem areas during the disassembly process. The radiograph can also be used as a means of determining lead deposition without opening the container.

The radiographic inspection of the catalysts was performed by the Quality Assurance Systems and Engineering Division at SwRI. This division conducts worldwide inspection of nuclear power plants, boilers and pipelines. The same standards and procedures used in radiographic inspection of welded joints in non-nuclear components such as pressure vessels and piping were used in radiographing the monolith catalysts.

To obtain the radiographs, the converter was placed in the bottom of a small (approximately 3 feet by 3 feet by 3 feet) lead lined chamber. The x-ray source was an x-ray generator tube at the top of the chamber. The film was placed directly under the converter (see Figure A-1). Initially, several exposures were made at different radiation outputs (i.e., different voltage inputs to the x-ray tube) to determine the optimum voltage setting and time of exposure for the type converter being radiographed. Two exposures of each converter were taken (one along the flat surface of the catalyst material and one perpendicular to it). The SwRI Radiographic Review Records for each individual catalyst inspected under this project are included in Appendix B. This record lists the x-ray tube voltage and current, exposure time, and other pertinent data and conditions. A representative radiograph of each converter lying flat with respect to the film is presented in Appendix B. Appendix B also contains the applicable portion of the SwRI Division 17 Operating Procedure for Radiographic Inspections. This operating procedure was followed for this project.

B. Disassembly of Whole Converters

Before the catalytic material could be divided into samples, the converter container had to be removed. This was accomplished by:

1. Cutting the end pieces from each converter container about one half inch from the face of the catalyst (See Figure A-2). The proper cutting location was determined from an inspection of the whole converter x-ray radiograph.

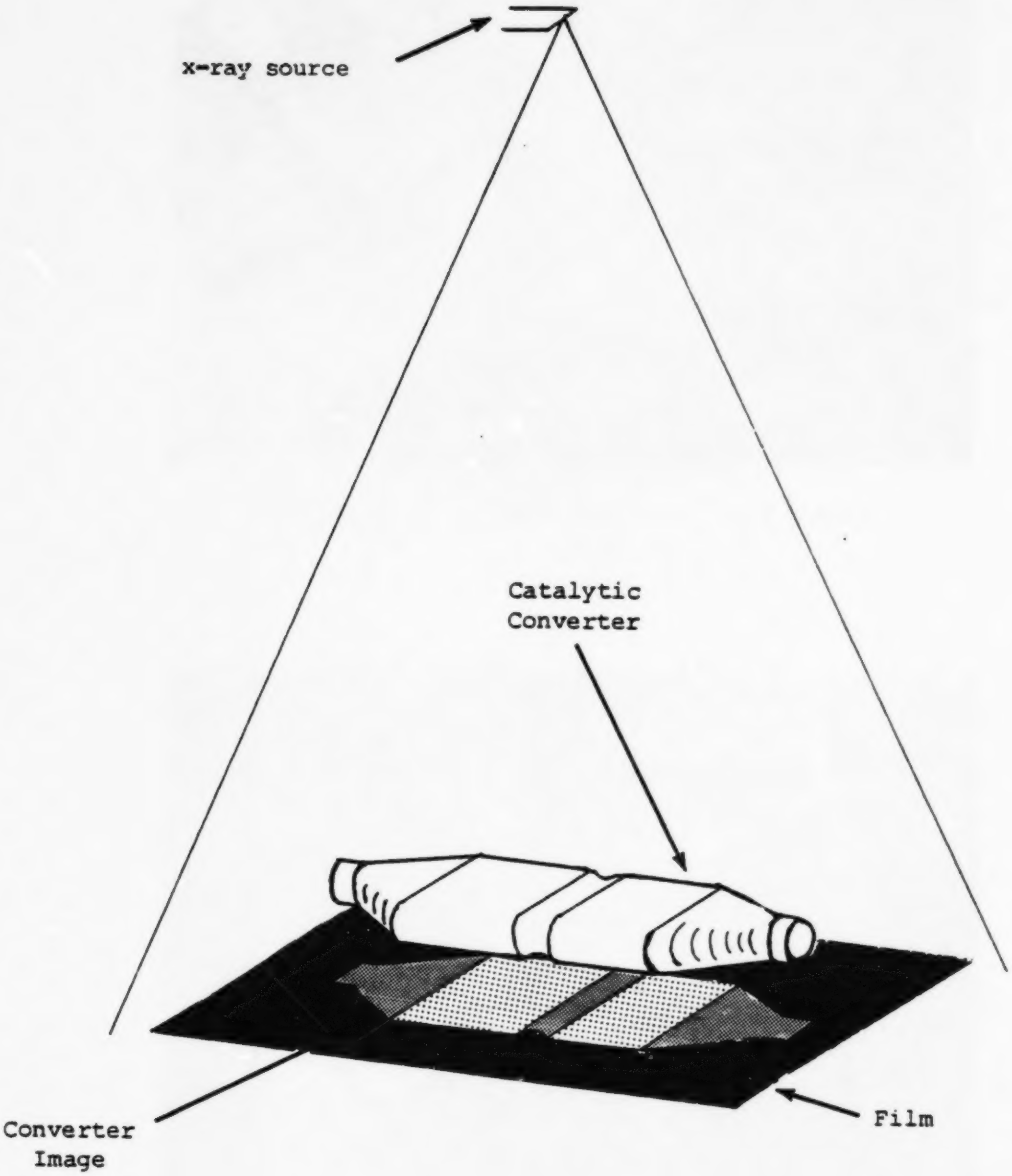

x-ray source
Catalytic Converter
Converter Image
Film

Figure A-1. Schematic representation of whole converter x-ray

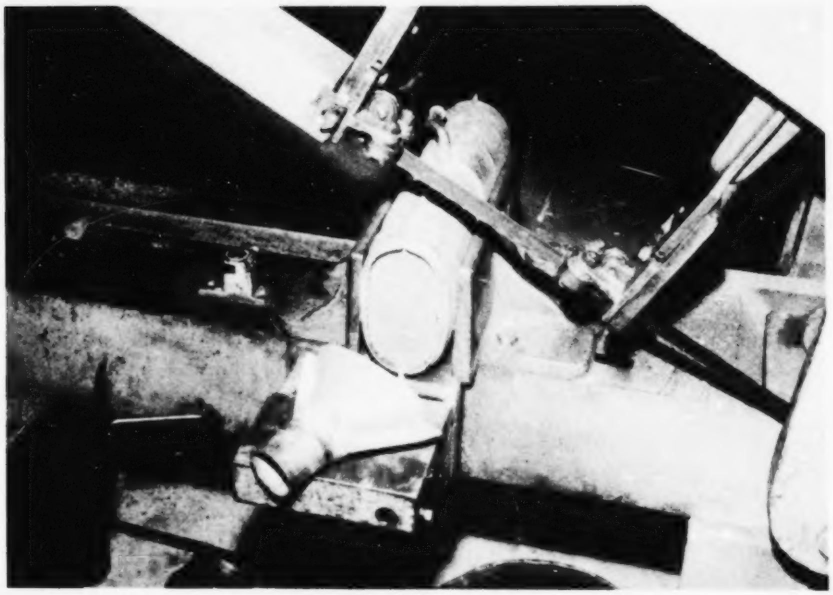


Figure A-2. Cutting end pieces from container

Figure A-3. Grinding Seam Weld

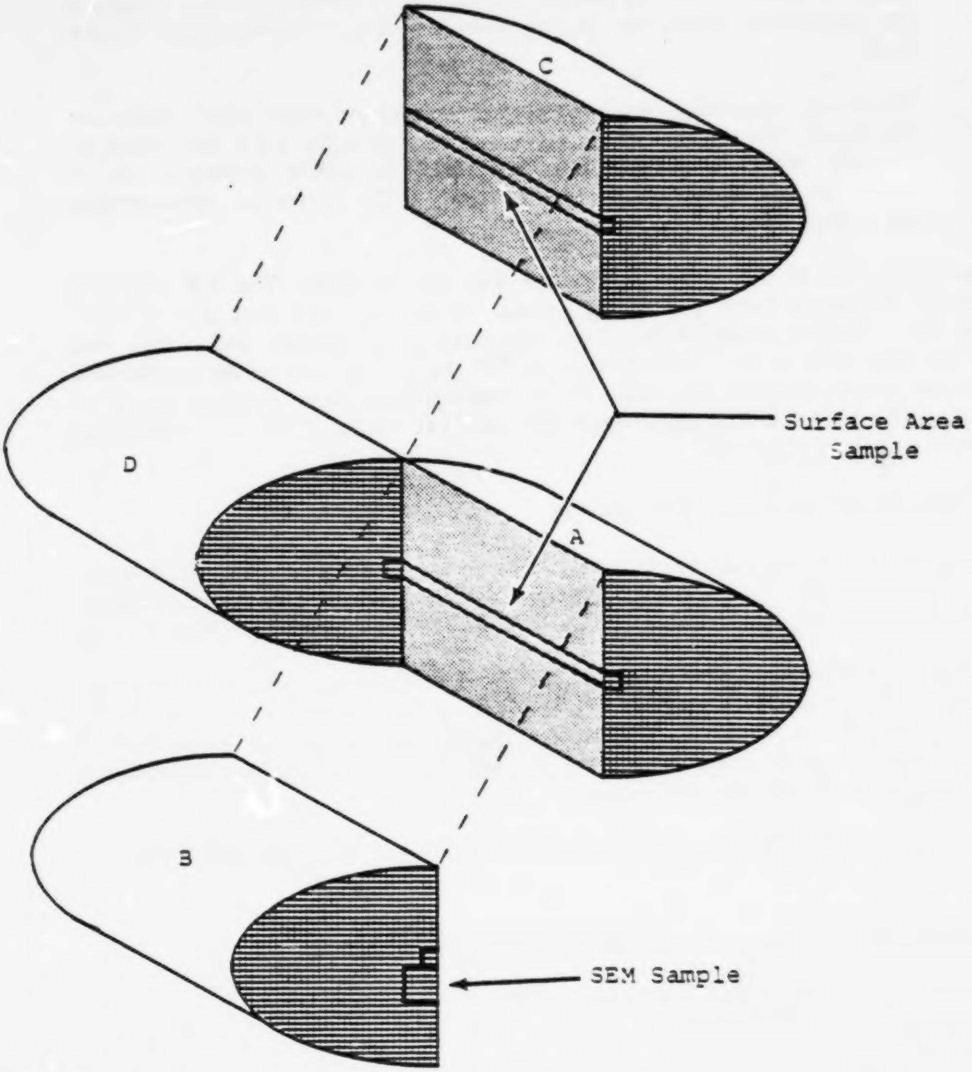

C
D
A
B
Surface Area Sample
SEM Sample

Figure A-4. Sectioning procedure for monolith catalyst samples

2. Grinding off the longitudinal seam weld. Each end of the converter container was taped to reduce the chance of damaging the catalytic material and preventing metal filings and other debris from entering the converter container during the grinding process. (See Figure A-3)

3. Removing carefully one side of the converter container. Again at this point, the whole converter x-ray radiographs were consulted to identify which catalysts had fractures or other problems which might be encountered during opening. The internal photographs were then taken of each catalyst.

The exception to the above procedure was sample -004. The VW catalyst was slightly different from the other seven. After the two end pieces were removed, the catalyst material was carefully pushed out of one end. This was possible because of the structure design of this particular converter container. As with the other converters, the x-ray radiographs were instrumental in determining the best method to remove the catalyst material without damaging the internal catalyst structure.

C. Sample Preparation and Distribution

Samples of the catalytic material were required for three different analytical procedures. These procedures and the location of the samples taken are presented in Table A-1. Each biscuit was quartered as shown in Figure A-4.

A 7 mm x 7 mm strip down the entire length was cut out of the center of each biscuit. This sample was then broken into lengths about 2 to 3 cm long. Sufficient pieces were required to give a total sample weight of more than 5 grams. These samples were labeled and sent to Micromeritics Instrument Corporation for BET Surface Area analysis.

TABLE A-1. ANALYTICAL PROCEDURES AND SAMPLE DISTRIBUTION

Test Procedures	Sample Location
BET Surface Area (specific area in m^2/g)	7 mm x 7 mm strip down entire length of the biscuit
SEM + surface x-ray fluorescence (pore structure and surface analysis for noble metals and poisons)	1 cm cube from front face of B
Bulk x-ray fluorescence (total noble metal and poison concentrations)	B and C ground up together and representative sample taken

The sample for the SEM, a 1 cm cube, was taken from the upstream face of the catalyst material. This method of sampling was chosen because the whole catalysts X-ray radiographs showed that the heaviest lead deposition was located in this area. Once the sample was prepared, it was sent to the U.S. Army Fuels and Lubricants Research Laboratory (Division 02) at Southwest Research Institute for analysis.

One front quarter and the rear quarter from the opposite side were selected for bulk x-ray fluorescence. These quarters were combined in a mortar and crushed by the pestle until a fine powder resulted. This method was chosen to average the noble metal and catalyst poisons over the entire catalyst. The resulting powder was sent the U.S. Army Fuels and Lubricants Research Laboratory (Division 02) at Southwest Research Institute for subsequent analysis.

D. Surface Area by BET Analysis

Automobile exhaust catalysts require large surface areas at the molecular level to provide sufficient exposure of the exhaust gas to the actual catalytic element. In automotive applications, the gamma form of alumina (Al_2O_3) is universally used as the material on which the noble metal catalyst is deposited, precisely because gamma alumina has a high surface area at the molecular level. In a used catalyst, this surface area can be reduced as a result of plugging by exhaust constituents, deposition of a catalyst poison, or by overheating the alumina (above 1000°C), causing a change in the alumina crystalline structure to the alpha alumina form. The alpha form of alumina has a lower surface area and is stable at low temperatures. Thus, once formed, the alumina retains the alpha structure even after cooling to normal catalyst operating temperatures. Measurement of the surface area of a used catalyst permits comparison with new catalysts to determine if there is still sufficient surface area for adequate exposure of the exhaust gases to the noble metal catalyst molecules.

Surface area is measured in terms of specific surface area (square meters per gram) by the BET physical adsorption method. The initials B.E.T. are for the three researchers, S. Brunauer, P.H. Emmett, and E. Teller, who first proposed the theoretical basis for calculating the volume of gas adsorbed on a surface in 1938.(9) The usual form of the equation resulting from that theory, called the BET equation, for adsorption of a gas at a constant temperature is:

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{(C-1)x}{v_m C}$$

where:

v_m = the volume required to cover the entire surface with a layer of the gas one molecule thick

v = the volume of the gas actually adsorbed on the surface

C = a dimensionless constant greater than one, and dependent on temperature only

x = the ratio of the pressure of the gas in the container to the saturation pressure of the gas, referred to as the relative pressure, P/P_o

A plot of $x/v(1-x)$ versus x, for various values of x is a straight line between $x = 0.05$ and $x = 0.3$. From the slope, S, and the intercept, I, of this straight line, both v_m and C can be determined, as follows:

$$v_m = \frac{1}{S+I} \quad \text{and} \quad C = 1 + \frac{S}{I}$$

Thus, if x and v are known, v_m, the volume of gas to cover the surface with a layer one molecule thick can be calculated. The total surface area of the solid is then calculated from the equation:

$$A = N_o v_m$$

where:

A = surface area of sample
N_o = Avogadro's number
= cross-sectional area of adsorbed molecule

There are a number of procedural methods and apparatus designs to infer v, the total volume adsorbed, at various measured values of x, the relative pressure ratio. Basically they fall into two classes: gravimetric and volumetric. Both methods use the BET equation above. They differ in that the gravimetric method measures the weight gain of the sample after adsorbing the nitrogen gas, while the volumetric method infers the amount of nitrogen adsorbed on the sample by Pv relationships. One example of a gravimetric technique is the ASTM "Standard Test Method for Surface Area of Catalysts," ASTM D3663-78. The procedure used in this project utilized a volumetric technique.

Since SwRI does not have the necessary equipment to perform the BET analysis, this work was subcontracted to Micromeritics Instrument Company, which manufactures equipment for BET analysis and provides a laboratory service using their equipment. The Micromeritics Digisorb 2600, a microcomputer controlled BET apparatus, was used to determine the specific surface area of all samples examined for this project. This instrument uses mixtures of nitrogen and helium gas cooled to liquid nitrogen temperature. Nitrogen will determine the area of the surface with any cracks or pores larger than the diameter of diatomic nitrogen. Since most of the exhaust gases are higher molecular weight than nitrogen, the reported surface area will be slightly higher than the surface area where catalysis takes place. this technique is the "state-of-the-are" technology. The degree of accuracy for this analytical procedure is about 1 m^2/g. The printout of the Digisorb 2600, showing the BET slope, intercept, C, and v_m for each of the catalyst samples are included in Appendix D.

E. Elemental Analysis by X-Ray Fluorescence

The ability of a catalytic converter to perform as designed can be adversely affected by certain elements that can be present in engine exhaust. One of the major "poisons" of automotive catalysts is lead. All gasoline, even that labeled "unleaded," contains some lead, so lead may even be present in catalysts that have been installed on vehicles which have never used leaded gasoline. Other elements that are deleterious to catalyst operation are: sulfur (S), phosphorus (P), manganese (Mn), calcium (Ca), and zinc (Zn). In addition, converter operation can be adversely affected if there is a loss of the actual noble metal catalyst itself from the converter substrate. To determine the extent of poisons and the amount of noble metal catalyst in the converter, a method of determining small quantities of various elements is required. For elemental analyses, this project used x-ray fluorescence (XRF) spectrometry techniques, also referred to as energy dispersive x-ray spectrometry (EDS). XRF is both a qualitative (element identification) and quantitative (amount of element) procedure.

The basic principle of XRF is that all elements will emit (fluoresce) x-rays when bombarded by high energy photons (x-rays or gamma rays). The energy level of the emitted x-rays in electron volts identifies the element. The reason for this can be seen by examining what happens to an atom when bombarded by photons.

Most of the photons impinging on an atom interact with the orbital electrons of the target atom in what may be considered as non-specific interactions, and result in little or no disturbance of the orbital electrons. However, some interactions result in the ejection of electrons from their orbits. The resulting vacancies, or holes, represent high energy, unstable states. If these orbital vacancies are in the innermost shells, electrons from outer shells cascade to fill them, resulting in a lower energy, more stable state. The energy released by the process produces x-rays. Each of the transitions which occur leads to the emission of x-ray energy at levels which are characteristic of the target element and the transition involved. This process is shown schematically in Figure A-5. By measuring the energy of the x-rays emitted, the element can be identified. By counting the number of x-rays at that energy level, the amount of the element can be determined by comparison to a standard. While the theory is simple, practical application requires a suitable detector and a computer to process the signal. A suitable detector was developed in the mid-1960's, and the development of the microprocessor in the 1970's made XRF equipment a laboratory reality.

For this project, the XRF analysis was performed by the Army Fuels and Lubricants Laboratory, operated by SwRI for the U.S. Army. The equipment used was an EXAM 902 detector together with an EDAX 707B analyzer, both manufactured by EDAX International, Inc. A photograph of the system is shown in Figure A-6. A schematic of the EDAX system is shown in Figure A-7.

One half of the catalyst material was ground into a course homogeneous powder with a large mortar and pestle. A portion of the sample was then ground into a very fine powder, mixed with an organic binder, placed in an aluminum cup, and pressed into a small briquette approximately 1 1/4 inches in diameter and 3/16 inches thick. The sample briquette is placed in the EXAM sample holder, the sample chamber purged with helium, and the x-ray bombardment begun. The stepwise procedure is listed in Table A-2. The run continues until a total of 40,000 counts (total of all energy levels) have been accumulated. This results in a determination of element quantity within approximately 2.5 percent. The counts at energy levels corresponding to the

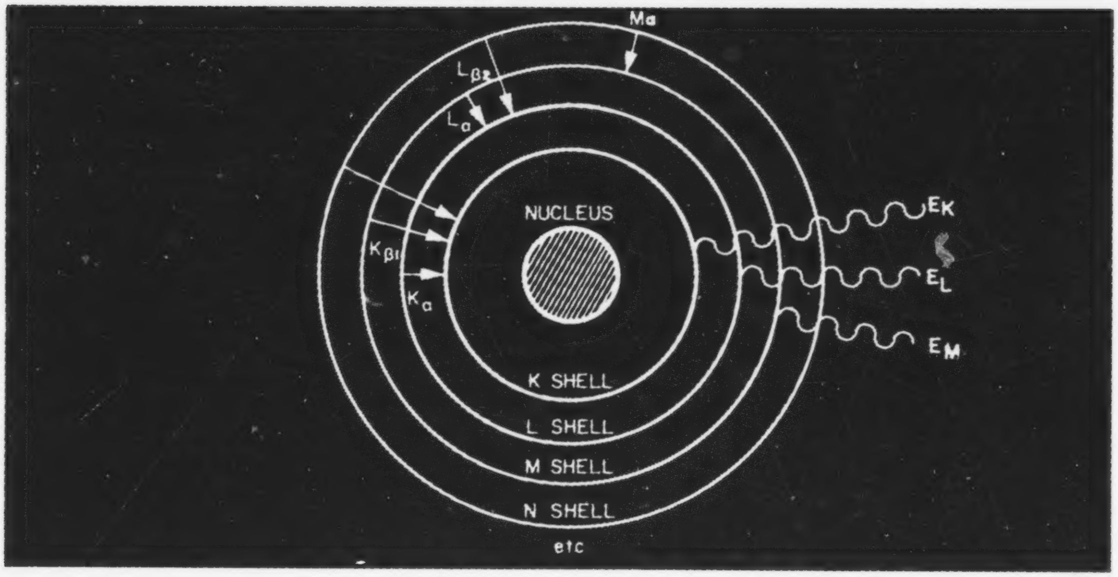

M_α
$L_{\beta 2}$
L_α
NUCLEUS
E_K
$K_{\beta 1}$
E_L
K_α
E_M
K SHELL
L SHELL
M SHELL
N SHELL
etc

Figure A-5. X-ray energy emitted by an atom that has lost electrons in the inner shells

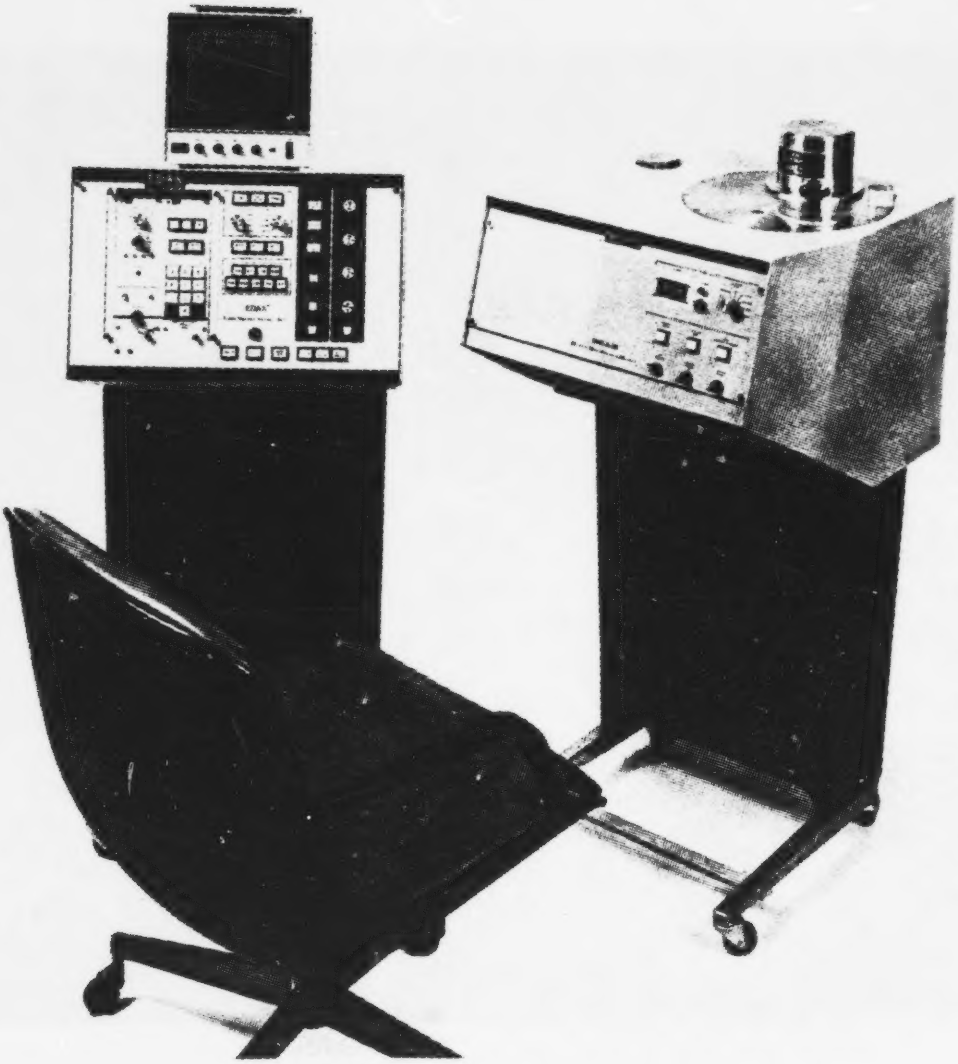
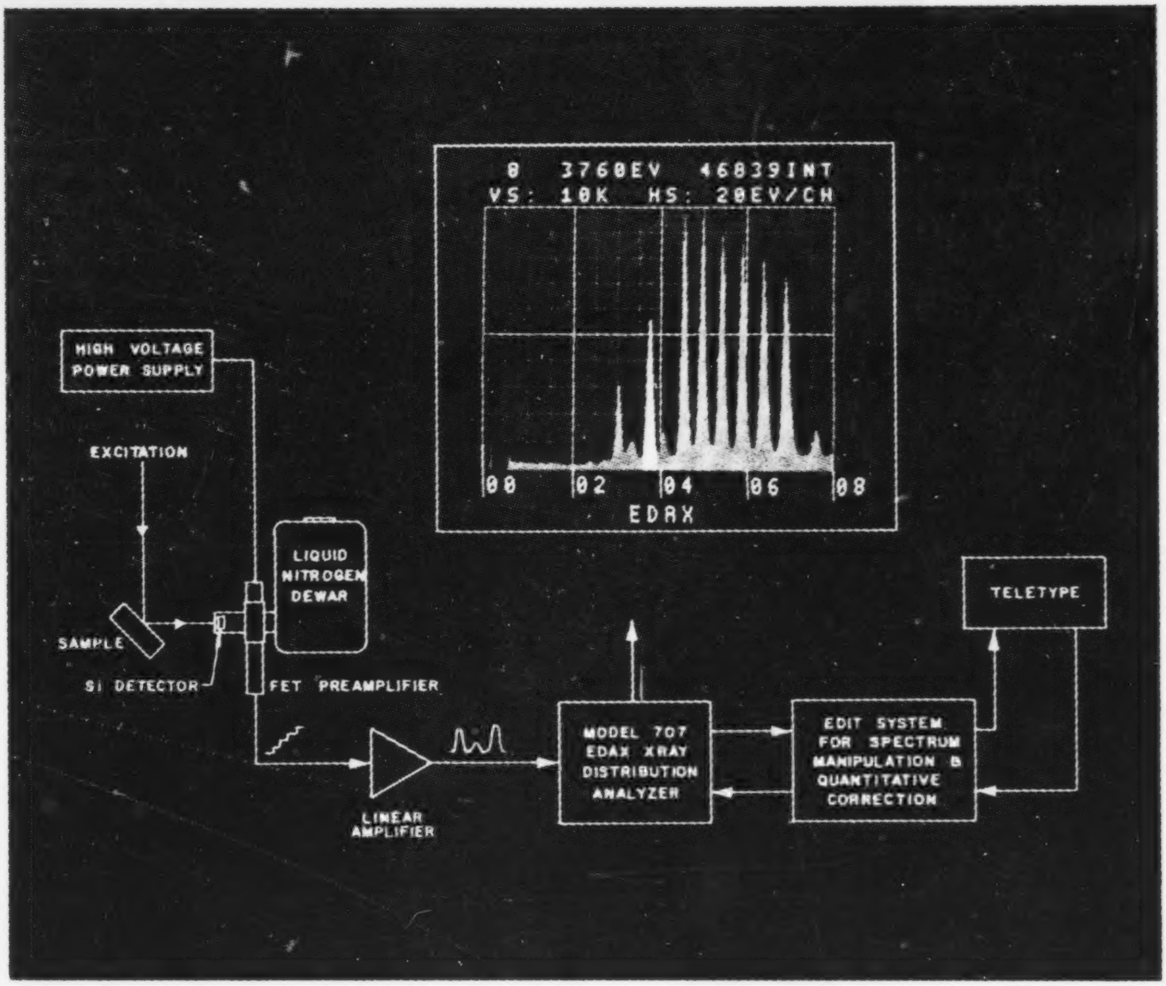


Figure A-6. EDAX/EXAM system



8 3760EV 46839INT
VS: 10K HS: 20EV/CH
00
02
04
06
08
EDAX
HIGH VOLTAGE POWER SUPPLY
EXCITATION
LIQUID NITROGEN DEWAR
SAMPLE
SI DETECTOR
FET PREAMPLIFIER
LINEAR AMPLIFIER
MODEL 707 EDAX XRAY DISTRIBUTION ANALYZER
EDIT SYSTEM FOR SPECTRUM MANIPULATION & QUANTITATIVE CORRECTION
TELETYPE

Figure A-7. Schematic of EDAX/EXAM system operation energy levels given off by the various elements sought are printed out by the computer. The energy spectrum from 1.28 to 11.02 KeV for each biscuit are included in Appendix D. The counts per second from the individual energy "lines" for each element in the sample are used to calculate the percent by weight from a regression equation developed from several runs of different concentrations of standards of each element. In this project, the percent by weight was obtained for the following elements: sulfur, phosphorus, calcium, manganese, zinc, nickel, lead, platinum, palladium, and rhodium.

TABLE A-2. STEPWISE PROCEDURES FOR ELEMENTAL ANALYSIS OF AUTOMOTIVE CATALYST SAMPLES BY XRF

1. Grind weighed amount of sample with 10 percent Somar-Mix powder added until a very fine, homogeneous powder is obtained.

2. Fill aluminum cap (Somar-Cap) with blended powder.

3. Press into pellet using hydraulic press.

4. Analyze samples using the energy dispersive x-ray system. Run analysis to 40,000 counts, total.

    a. equipment: EXAM 902 detector
       EDAX 707B analyzer

    b. conditions for elements S, P, Ca, Mn, Zn, Pb and Pt:

       Silver x-ray source tube
       3 minute purge with helium
       20 Kv voltage
       64 a current

    c. conditions for elements Pd and Rh:

       Gold x-ray source tube
       3 minute purge with helium
       29 Kv voltage
       8 a current

5. Enter counts per second over background obtained for each element in a sample into the XRF regression programs, using coefficients obtained from multipoint analysis of standards.

6. Standards are run using procedure steps 1 and 4 above. Standards are prepared by weighing out pure oxide forms of each element in a matrix of 20 percent aluminum oxide (to approximate the catalyst base material) and Somar-Mix briquetting material.

The repeatability of the analytical system was determined with a series of five repeat runs on a sample of known initial concentrations for the various elements. This sample was blended with clean catalyst substrate material (alumina) obtained from W. R. Grace to simulate as close as possible the conditions of a catalyst sample. The results of the repeatability experiment are presented in Table A-3. The standard deviation of the five repeat runs was less than 1 percent except for the elements platinum and sulfur. Sulfur was the worst with a standard deviation of 0.041. The percent change of the mean values for the five repeat runs to the actual concentration in the sample was below 5 percent except for sulfur with -14.2 percent. This was probably due to the overlap of energy levels when lead and sulfur are present in the same sample.

TABLE A-3. REPEATABILITY EXPERIMENT FOR X-RAY FLUORESCENCE

Element	Repeat Runs, wt. % 1	2	3	4	5	Mean	Standard Deviation	Actual Conc.	Percent Change
P	0.265	0.268	0.264	0.273	0.256	0.265	0.006	0.27	-1.9
S	0.303	0.226	0.217	0.292	0.290	0.266	0.041	0.31	-14.2
Ca	0.048	0.054	0.051	0.052	0.046	0.050	0.003	0.05	0.0
Mn	0.381	0.394	0.393	0.380	0.379	0.385	0.007	0.38	1.3
Ni	0.247	0.258	0.258	0.253	0.244	0.252	0.006	0.25	0.8
Zn	0.082	0.083	0.085	0.083	0.081	0.083	0.001	0.08	3.8
Pb	0.177	0.181	0.194	0.182	0.170	0.181	0.009	0.18	0.6
Pt	0.298	0.335	0.309	0.312	0.315	0.314	0.013	0.30	4.7

F. Examination by Scanning Electron Microscope

The ability of a catalytic converter to function correctly is very much dependent on the microscopic topography of the catalyst substrate. A scanning electron microscope (SEM) was used to examine this topography. The scanning electron microscope is simple in principle, but complex in execution. Interpretation of results for the most part, follows from observations made with the naked eye or optical microscopes. Thus, it is not incorrect to say that the SEM is an extension of the human eye; all that one is doing is increasing the magnification and resolution of the eye. The SEM bombards the sample with electrons rather than with visible light. When using electrons rather than visible light, two advantages occur: a wavelength much shorter than visible light is generated and the source is nearly all the same wavelength. Shorter wavelengths permit higher resolution and monochromatic radiation permits simpler lens design. The electrons are focused by either electrostatic or electromagnetic lenses. The lenses are arranged in a typical SEM column as shown in Figure A-8. Control of the intensity, wavelength and penetration of the electron beam gives a flexibility to the SEM for which there is no parallel in optical microscopy. This flexibility does add to the complexity of operation of the SEM, however.

The specimen illuminated by the electron beam both scatters and absorbs the electrons. The absorbed energy is reemitted as x-ray, secondary electrons, and auger electrons. Figure A-9 illustrates this process. Surface topography contrast is usually determined by use of secondary electrons, those very low energy electrons which can penetrate only a small amount of material, thus originating close to the surface. Secondary electron detectors are usually

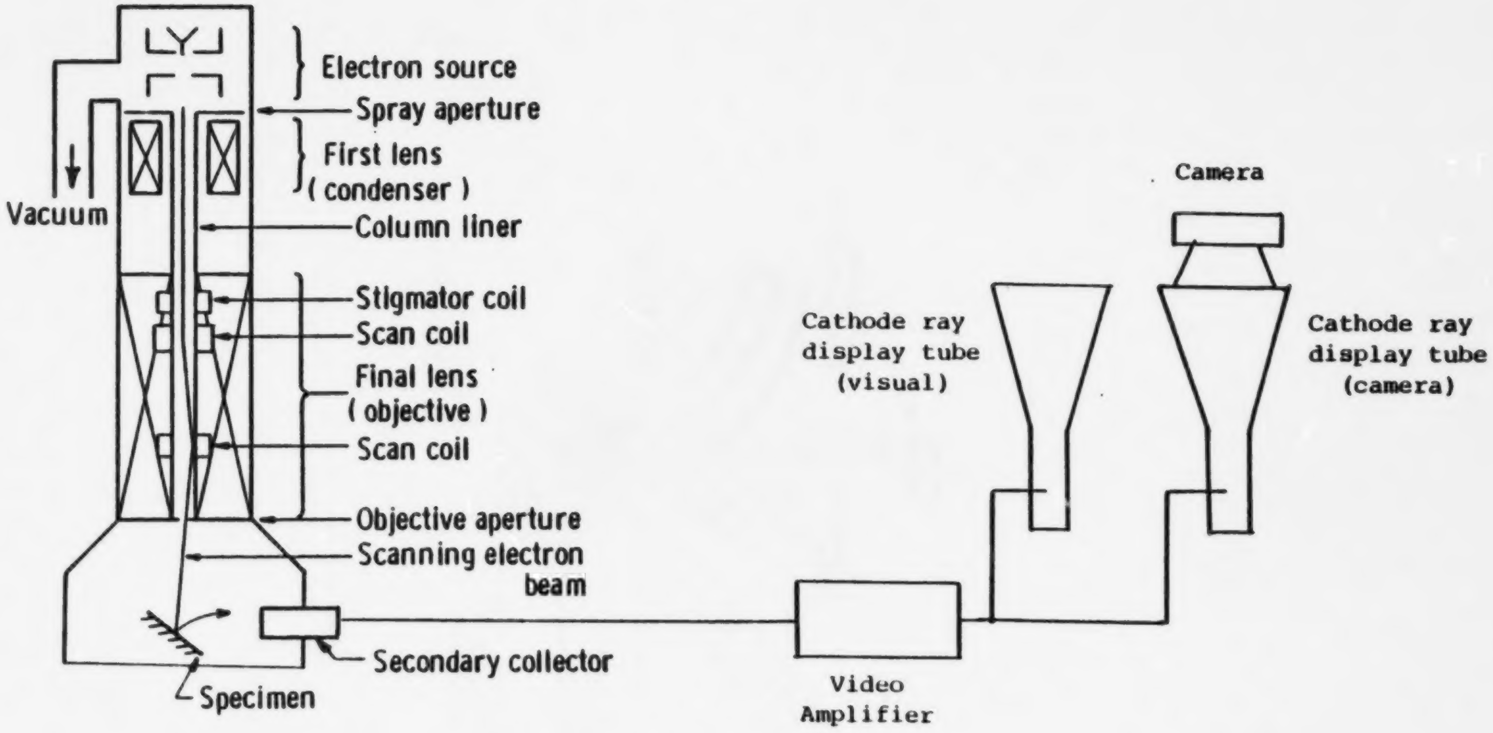

Electron source
Spray aperture
First lens
(condenser)
Vacuum
Column liner
Stigmator coil
Scan coil
Final lens
(objective)
Scan coil
Objective aperture
Scanning electron beam
Secondary collector
Specimen
Video Amplifier
Cathode ray display tube (visual)
Camera
Cathode ray display tube (camera)

Figure A-8 . Schematic of scanning electron microscope

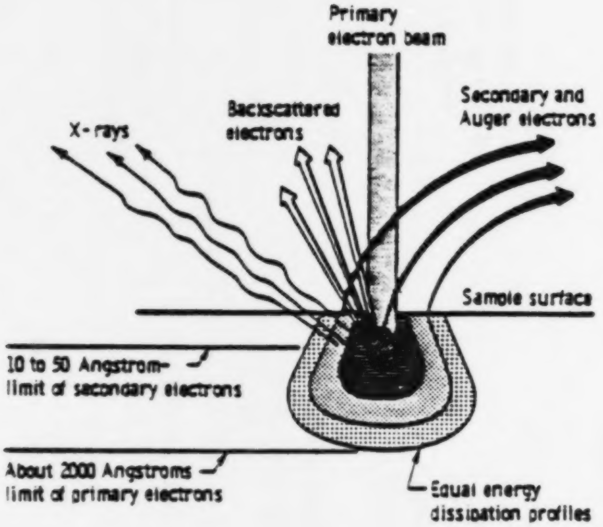

Primary
electron beam
Backscattered
electrons
Secondary and
Auger electrons
X-rays
Sample surface
10 to 50 Angstrom-
limit of secondary electrons
About 2000 Angstroms
limit of primary electrons
Equal energy
dissipation profiles

Figure A-9. Forms of emitted energy from a specimen in a SEM photomultiplier tubes located to the side of the sample as shown in Figure A-8.

Because alumina is a good insulator, when the electron beam strikes the catalyst sample for any period of time, a static charge is built up. This static charges completely "washes out" any detail in the cathode ray tube display. To prevent static charge buildups, after the sample had been mounted on an SEM sample holder, the sample and sample holder were coated with a thin layer (several molecular layers thick) of gold by vapor deposition, to ground the sample.

An AMR Corporation, Model AMR 1200 scanning electron microscope was used to examine the catalyst samples from this project. Figure A-10 is a photograph of the AMR 1200. This SEM is equipped with an automatic filament control. Operator control is needed only to select one of the three acceleration voltages available (5, 15, or 30 kV). The operator can also select one of three final aperatures for control of depth of focus, incident current and resolution. For this project, an acceleration voltage of 30 kv was used. The smallest (100 micron) final aperature was used for best visual resolution. A sample tilt angle of 30° was generally used. Appendix F contains micrographs of typical surfaces for each of the catalysts.

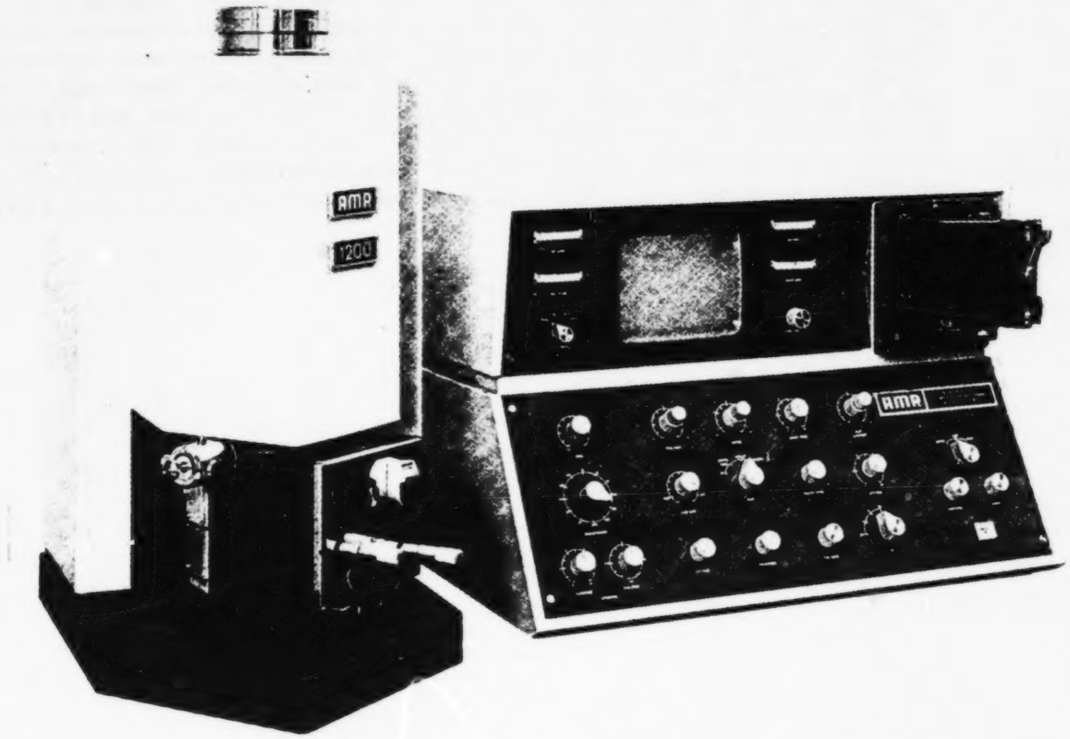

AMR
1200
AMR

Figure A-10. Photograph of AMR Corporation, Model AMR1200 scanning electron microscope

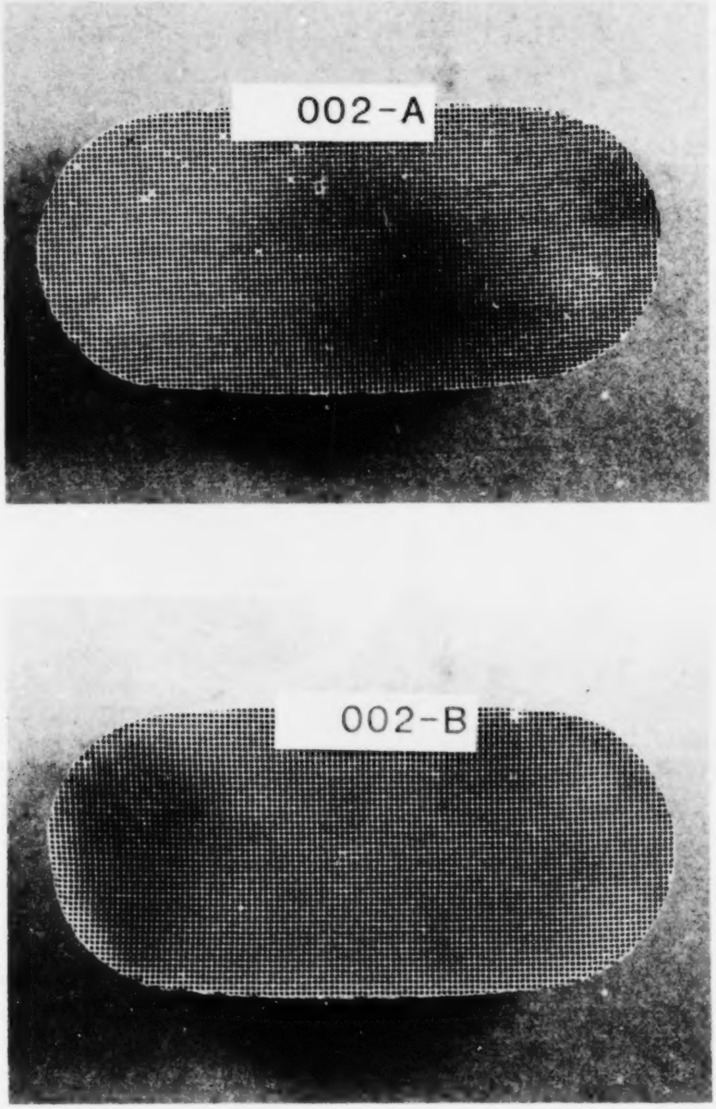


Figure A-11. Front face view of 002

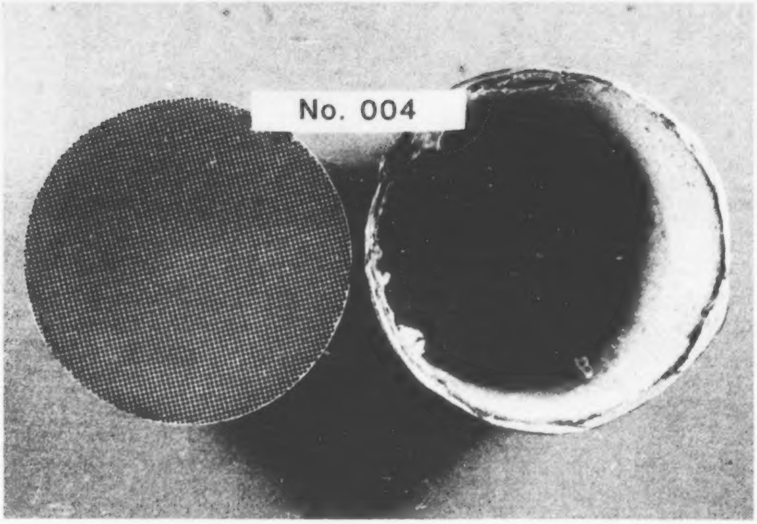


Figure A-12. Front face view of 004

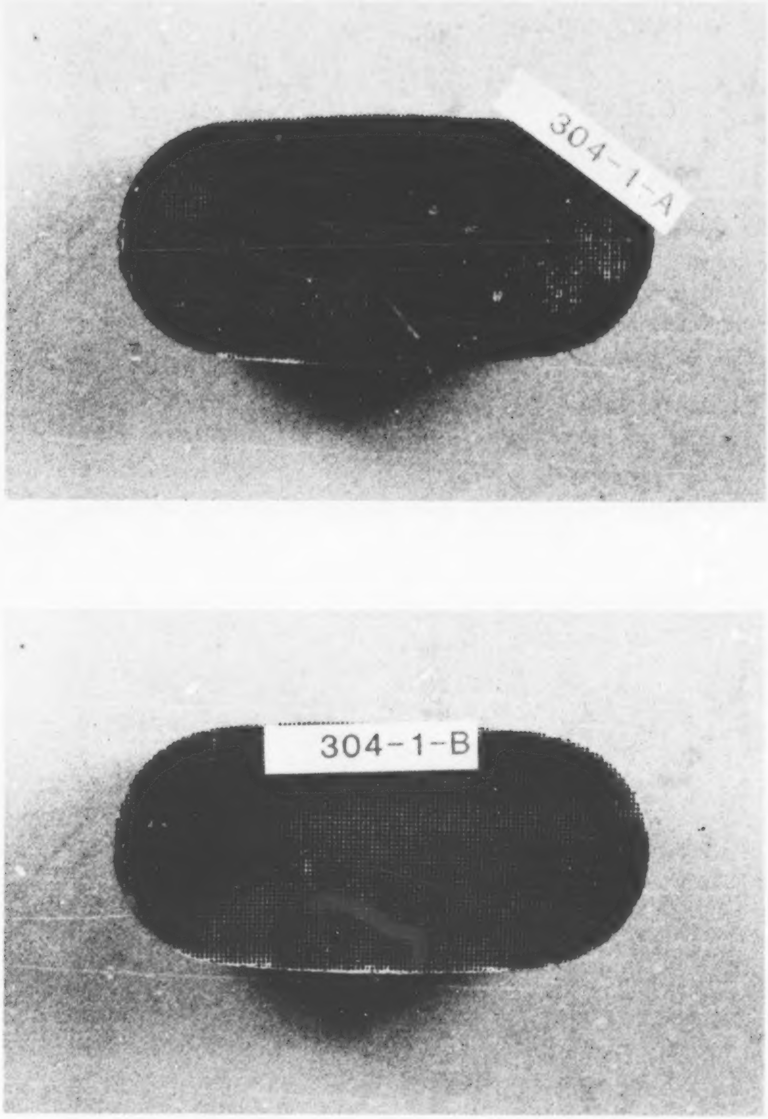

304-1-A
304-1-B

Figure A-13. Front face view of 304-1

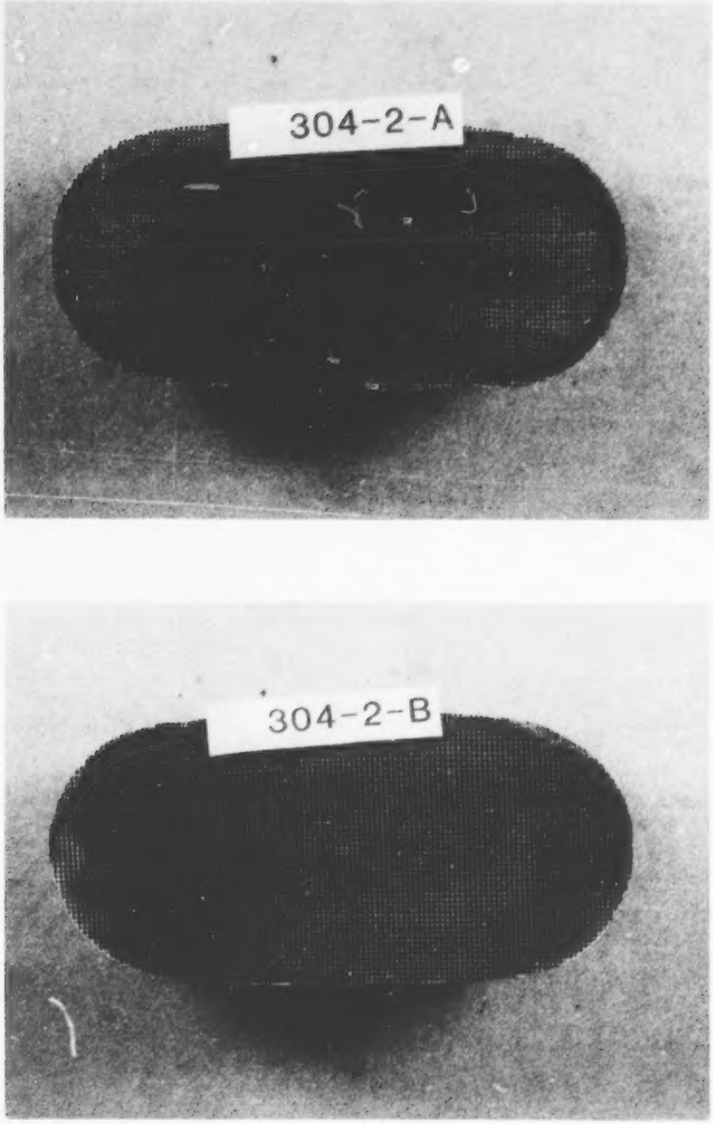

304-2-A
304-2-B

Figure A-14. Front face view of 304-2

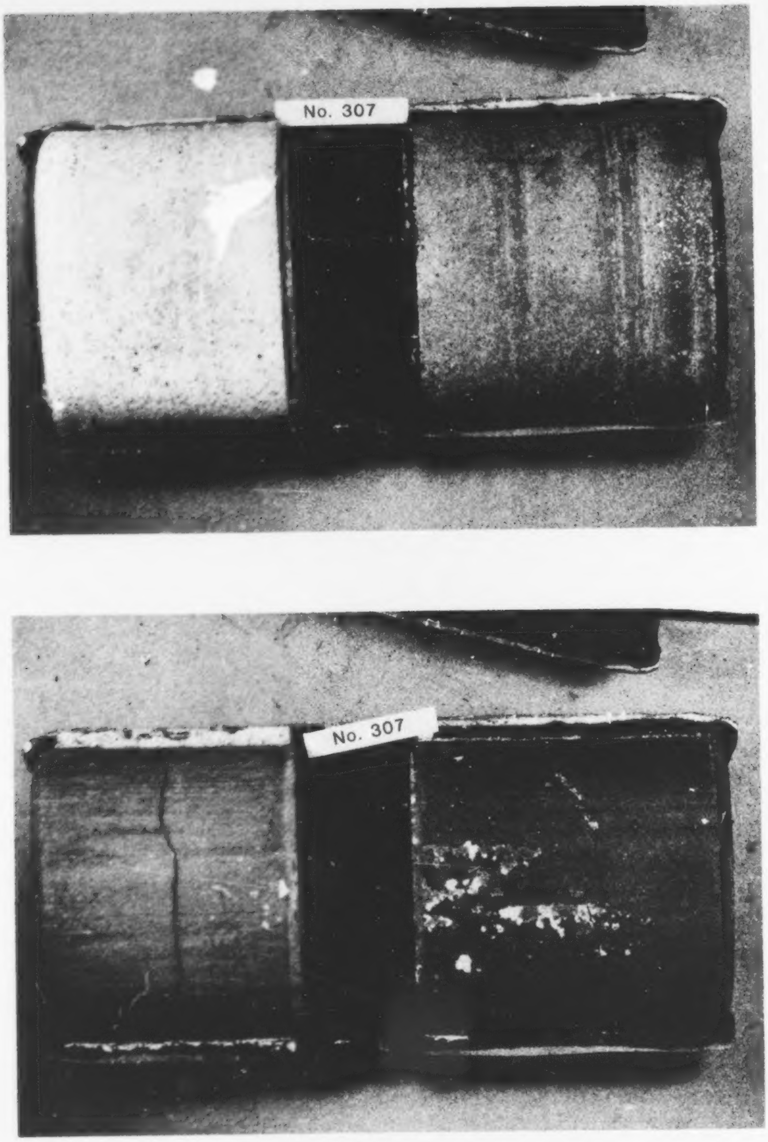

No. 307
No. 307

Figure A-15. Side view of 307

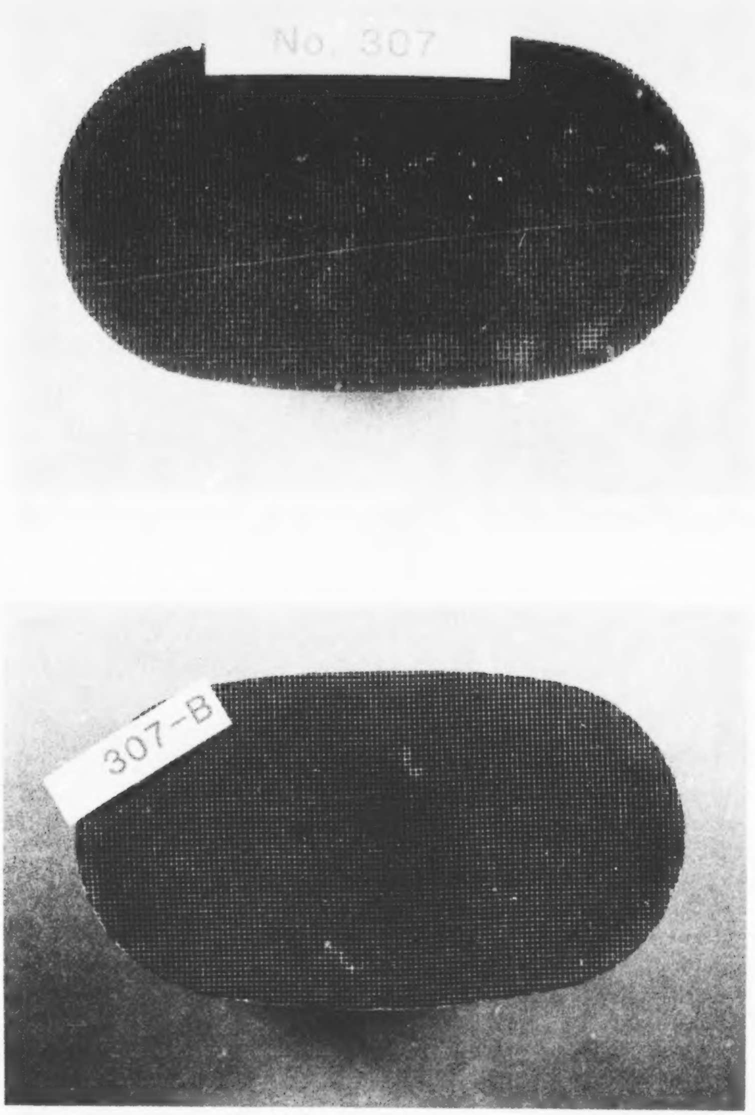


Figure A-16. Front face view of 307

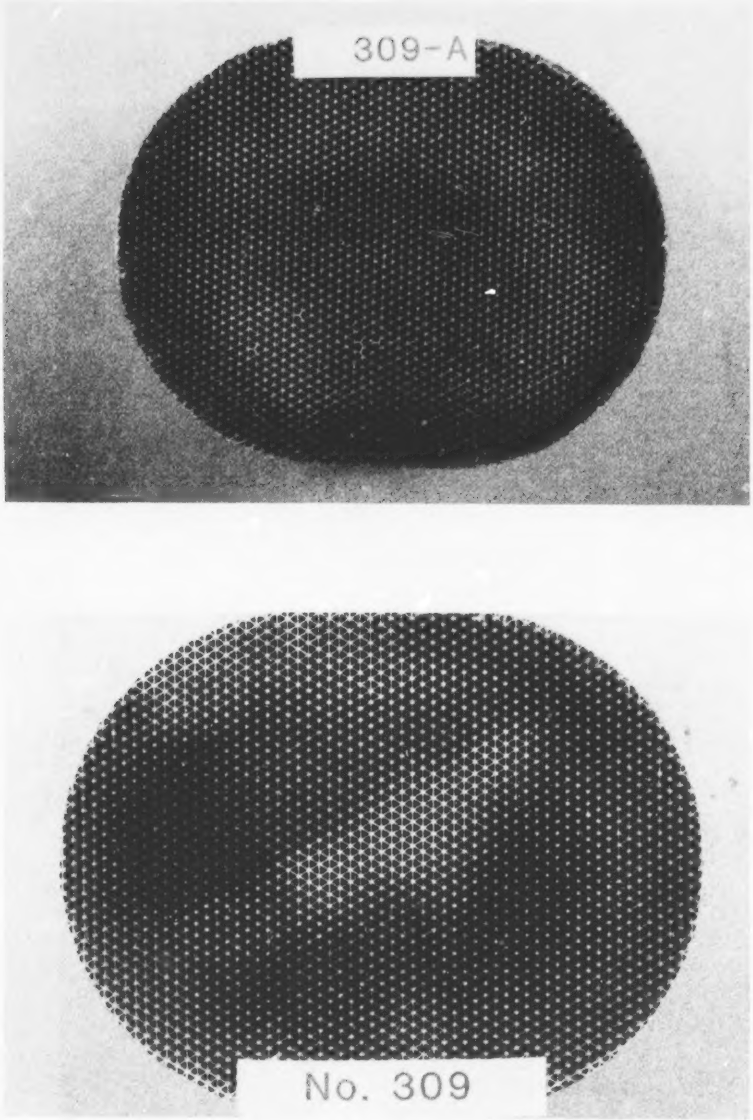


Figure A-17. Front face view of 309

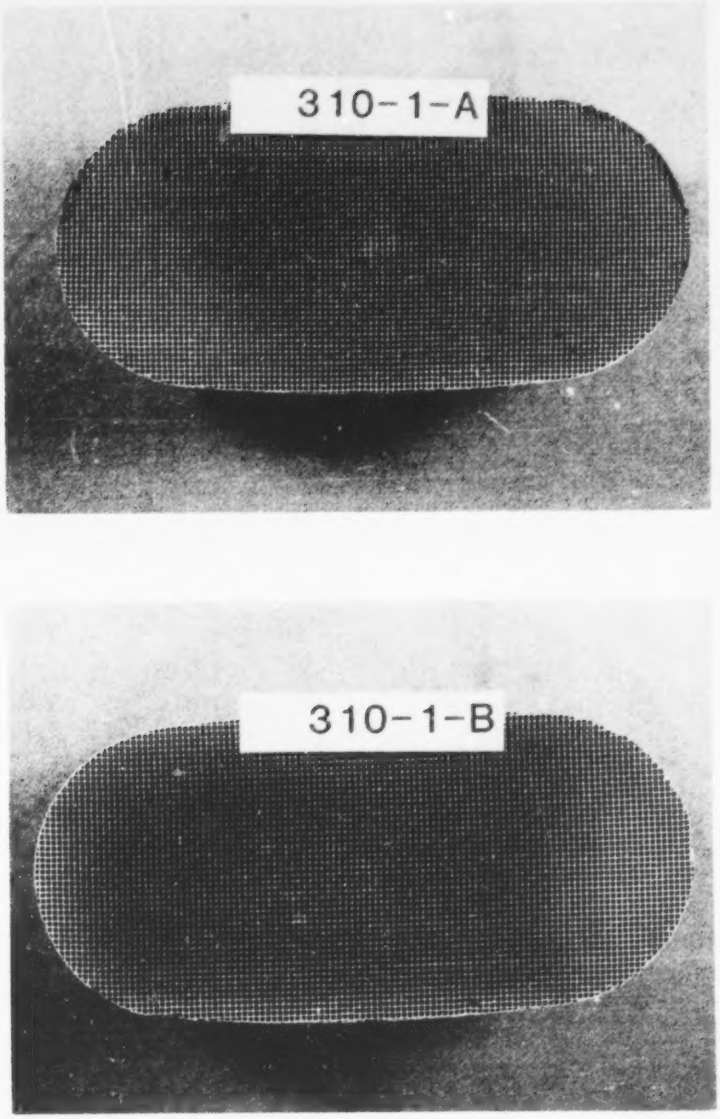

310-1-A
310-1-B

Figure A-18. Front face view of 310-1

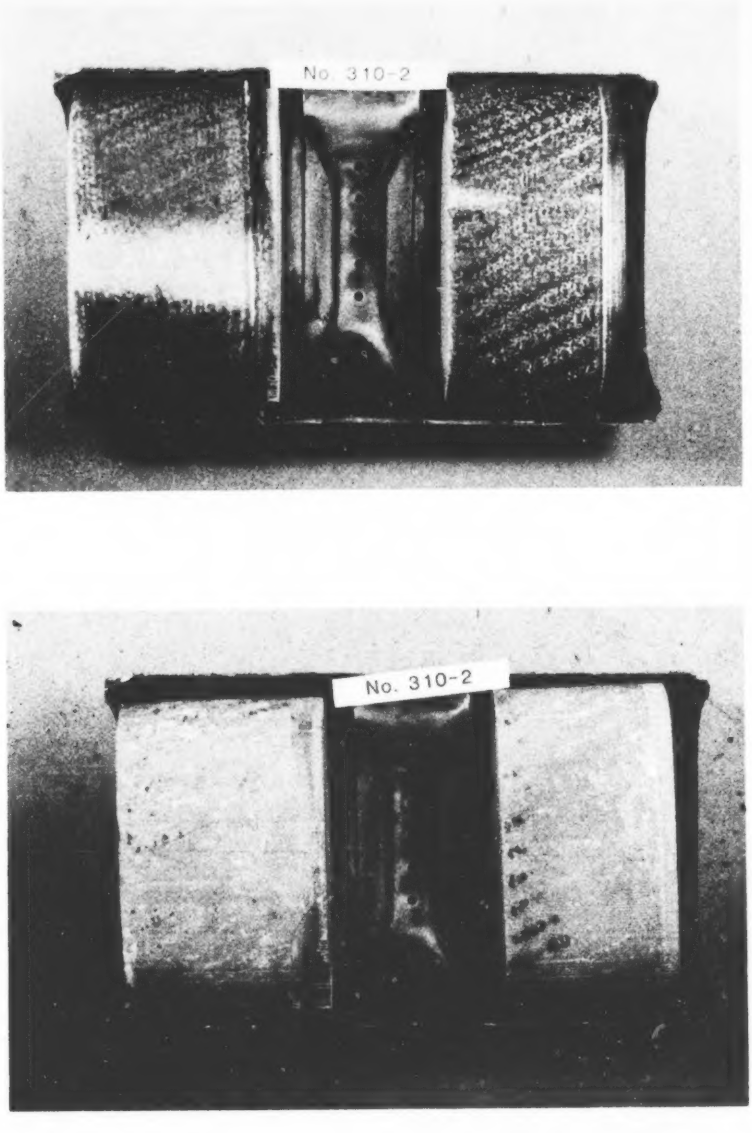

No. 310-2
No. 310-2

Figure A-19. Side View of 310-2

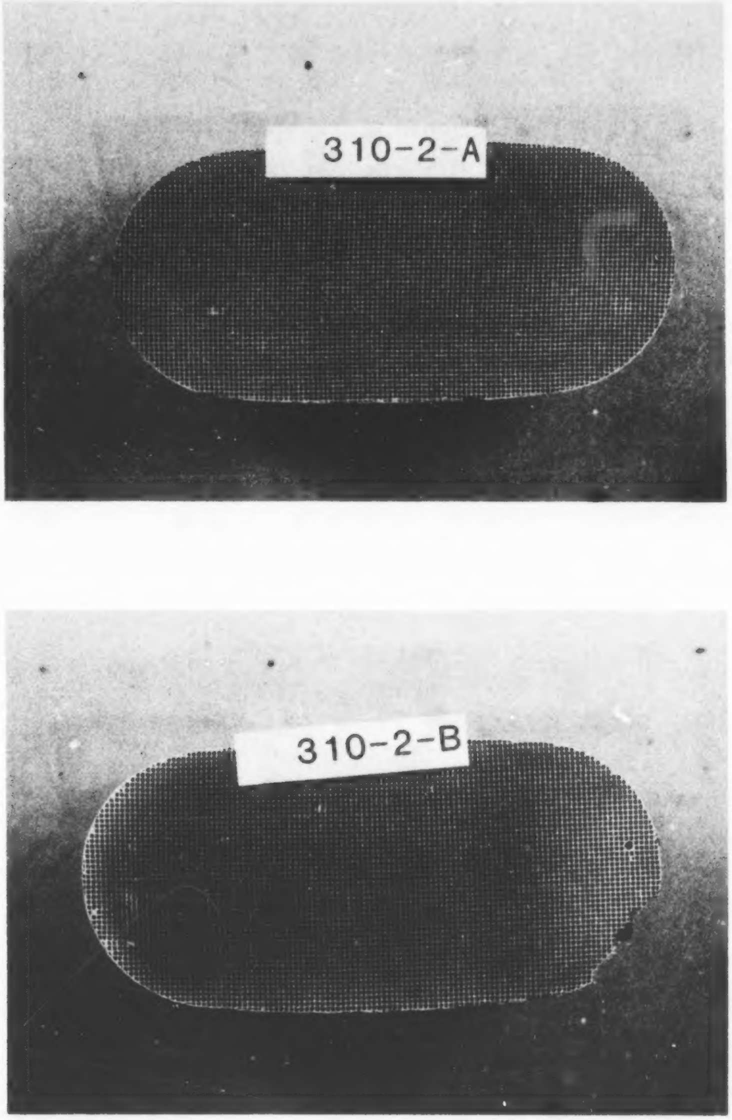

310-2-A
310-2-B

Figure A-20. Front face view of 310-2

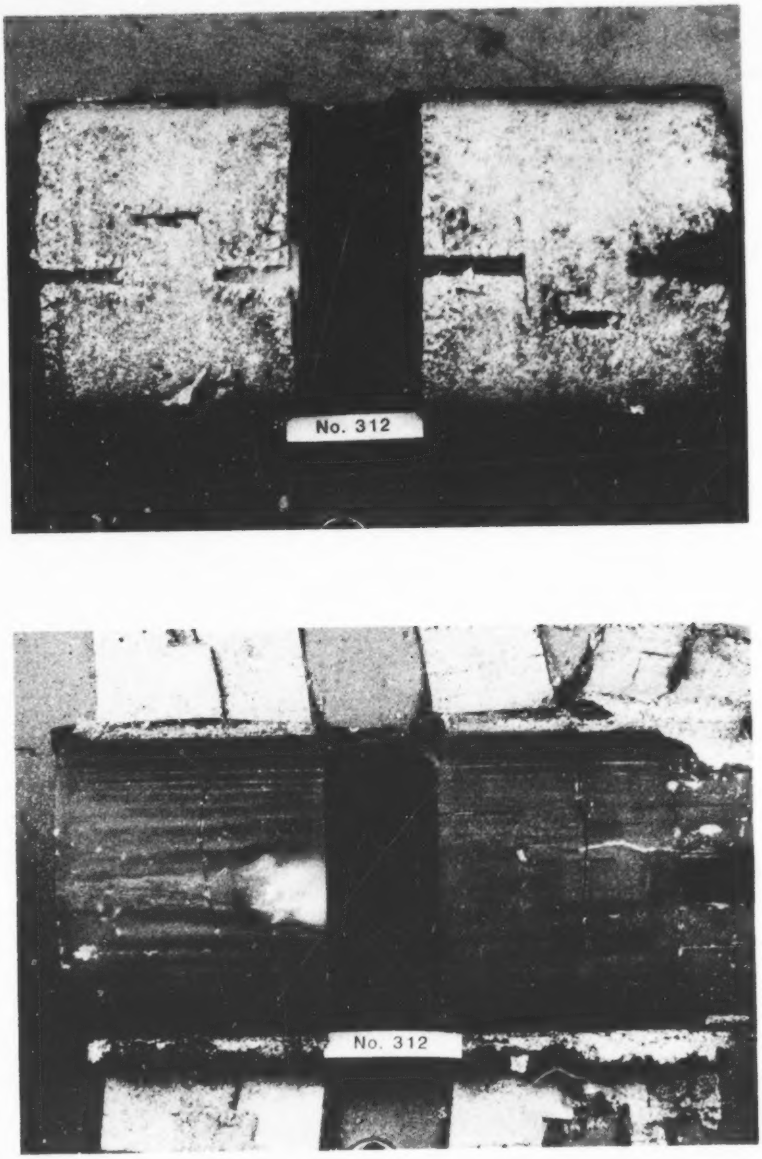

No. 312
No. 312

Figure A-21. Side View of 312

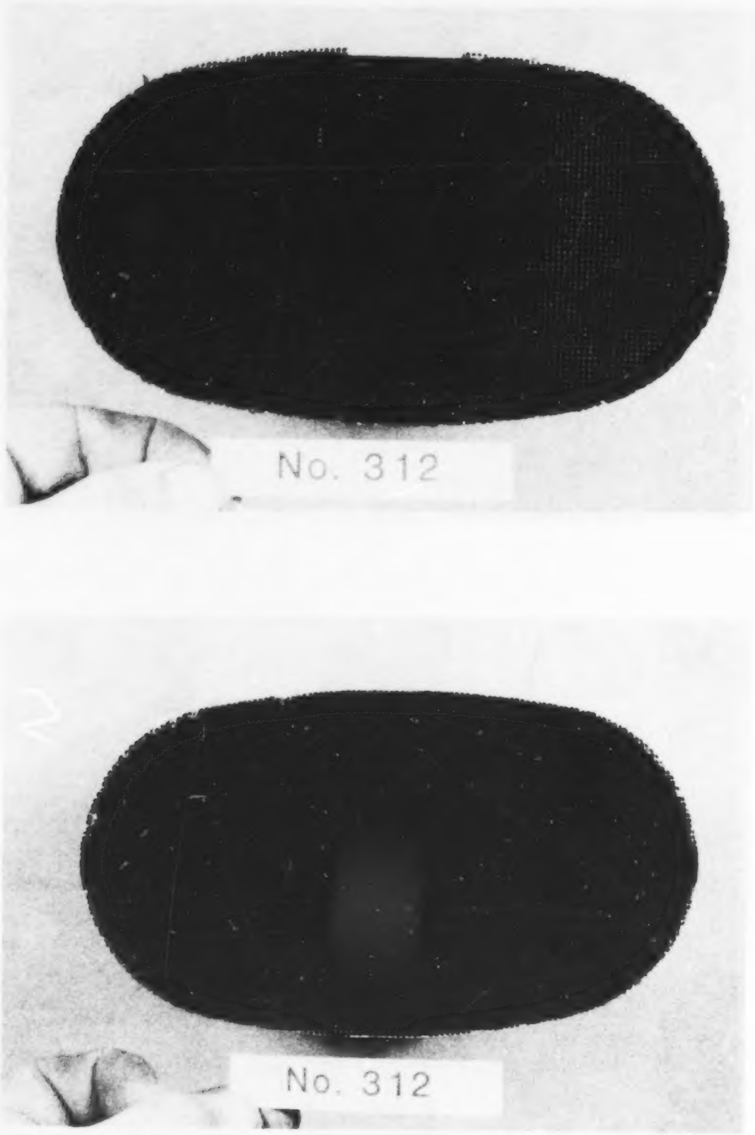

No. 312
No. 312

Figure A-22. Front face view of 312

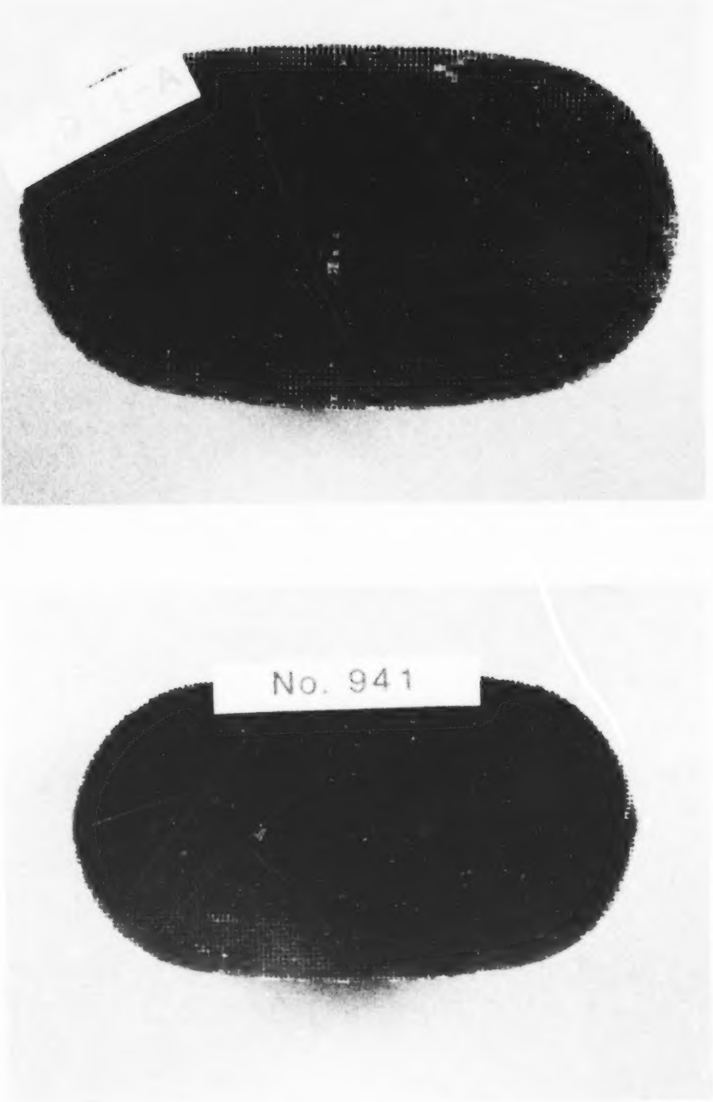


Figure A-23. Front face view of 941

APPENDIX B

RADIOGRAPHIC RECORDS AND RADIOGRAPHS OF WHOLE MONOLITH CONVERTERS

SOUTHWEST RESEARCH INSTITUTE
DIVISION 17
OPERATING PROCEDURE

OP-17-40-001
Revision 1
July 1982
Page 1 of 15

RADIOGRAPHIC INSPECTION OF NON-NUCLEAR COMPONENTS

1. PURPOSE

1.1 This procedure describes the requirements for shop or field radiographic examination of welded joints in non-nuclear pressure vessels, piping, nozzles, and similar configurations. This procedure complies with the minimum requirements of the ASME Boiler and Pressure Vessel Code, Sections V and VIII, 1980 Edition, plus addenda through Winter 1981.

1.2 This procedure shall be applicable to welds containing consumable inserts, back-up rings, or strips where radiography is required by specification, procedure, code, or contracted agreement.

2. REFERENCE

2.1 ASME Boiler and Pressure Vessel Code, Section V, Articles 2, 1980 Edition plus addenda through Winter 1981.

2.2 When the requirements of this procedure and ASME Section V meet or exceed the requirements of other codes or standards, including but not limited to ASME Section VIII, Division 1 and 2, NAVSHIPS 0900-006-9010, American Welding Society AWS D1.1, American Bureau of Shipping, and American Petroleum Institute API 1104, the acceptance criteria may be included in this procedure as an appendix.

2.3 Any special requirements necessary to meet the referenced code or standard may be included in the appropriate appendix and will become a part of this procedure for radiographic examination of such components.

3. PERSONNEL

3.1 All personnel performing radiographic examinations shall be qualified in accordance with ASNT SNT-TC-1A.

4. RESPONSIBILITY

4.1 The Director of the Department of Research and Development within the Quality Assurance Systems and Engineering Division shall be responsible for the initiation of the procedure.

WRITTEN BY	DATE	TECHNICAL REVIEW	DATE	COGNIZANT DIRECTOR	DATE	SS
	7/		7/82	R. Whiting	7/82	CK

6.1.4 Film brand or type and number of films in cassette.

6.1.5 Type and thickness of intensifying screens and filters.

6.1.6 Blocking or masking techniques, if used.

6.1.7 Minimum source-to-film distance (SFD).

6.1.8 Sketch showing exposure geometry.

6.1.9 Description of or reference to the welding procedure, where applicable.

6.2 Radiographs demonstrating the exposure techniques shall be maintained and kept on file.

6.3 In cases where the production radiograph is used as the radiographic procedure qualification, the radiographic film shall be filed in accordance with the contract requirements.

6.4 An exposure technique shall be established for each component radiographed. A new technique shall be established for the following changes:

6.4.1 Each different type of radiation source used; i.e., the use of different X-ray voltages or a change in type of isotope.

6.4.2 A change to a faster film.

6.4.3 The use of fewer or thinner lead screens.

6.4.4 Each change in basic exposure geometry; i.e., single wall, double wall, elliptical exposure, step-weld joint, etc.

6.5 The applicable exposure techniques shall be referenced on the Radiographic Interpretation Report of each weld radiographed. Figure 1 is a typical Radiographic Interpretation Report Form.

7.0 MATERIAL THICKNESS AND TYPE

7.1 This procedure covers the material thickness range from 0.2 to 6.0 inches, unless specifically prohibited.

12.2 Radiographs shall be made of completed welds in accordance with this procedure. However, this does not preclude the use of radiography at other stages of fabrication such as partially completed welds or welds during repair operations.

13. FILM

13.1 Types 1 and 2 Radiographic Film, such as Eastman Kodak M, T, AA, or equivalent, shall be used; the type to be used is dependent on the part being radiographed.

14. INTENSIFYING SCREENS

14.1 A front and a back lead intensifying screen shall be used in all exposures above 150 KV and for all isotope exposures. When necessary, lead screens may be used for exposure at or below 150 KV. Fluorescent screens shall not be used.

15. FILM AND SOURCE PLACEMENT

15.1 Film cassettes shall be loaded with one film or two films with "sandwich" construction of lead screen and film. Screen thicknesses shall be appropriate for the energy level of the radiation source.

15.2 The film cassette shall be as close to the surface of the area of inspection as practicable.

15.3 The cassette shall be firmly fixed and maintained to the surface of the component during exposure.

15.4 The source shall be free of movement during exposure of film.

16. EXPOSURE

16.1 The exposure time shall be such as to produce a film density in accordance with Section V, Paragraph T-234, and shall, in no case, be less than 2.6 for composite viewing or exceed 4.0. The density shall be evaluated by using an ASA density comparison strip or a densitometer.

16.2 The geometric unsharpness of the resultant radiographic image shall not exceed the requirements of ASME Section V, Paragraph T-251, when required by the referencing Code.

16.3 A lead symbol "B" is to be used as a back scatter check; it shall be attached to the back side of the cassette in accordance with Section V, Paragraph T-235.

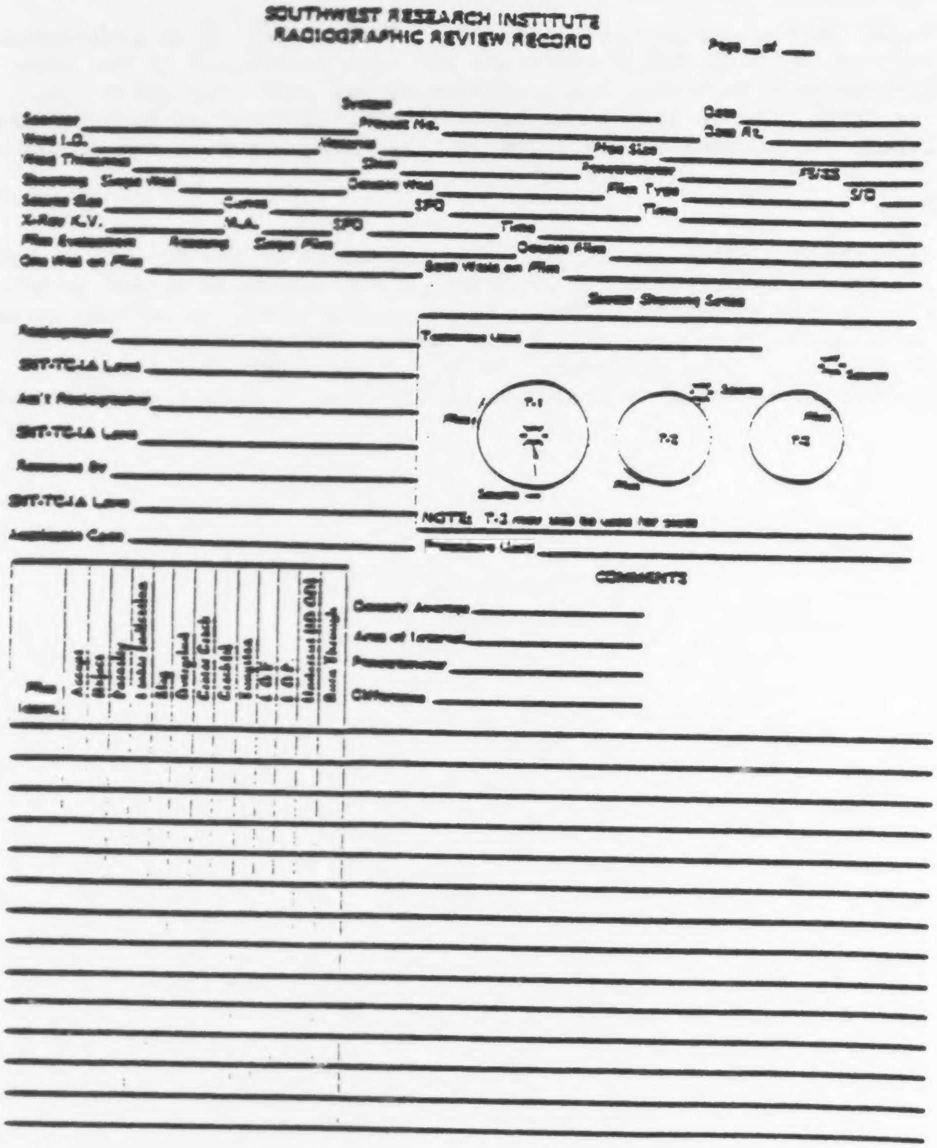
WRITTEN BY	DATE	TECHNICAL REVIEW	DATE	COGNIZANT DIRECTOR	DATE	SS
	[illegible]		7/82	Allen R. Whiting	7/82	C.K

21. REEXAMINATION AFTER REPAIRS

21.1 Welds showing unacceptable defects shall be repaired in accordance with the welding repair procedure and then reexamined by the same radiographic technique and procedure as was used originally. All resulting film records shall be permanently identified as subsequent repair radiographs and retained as a permanent part of the record.

22. RECORDS

22.1 Radiographic films and records shall be filed by the Project Manager for the period required by contract unless otherwise agreed to by the interested parties. Exposure conditions shall be written on an accompanying form essentially the same as the one shown in Figure B-1 of this procedure. An accurate sketch of the radiographic setup shall be presented at the time of film interpretation.



SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page __ of ___

Project No. ____
Date ____
Weld I.D. ____
Pipe Size ____
Film Type ____ S/D ____
X-Ray K.V. ____ M.A. ____ SFD ____ Time ____

Radiographer ____
SNT-TC-1A Level ____
Ass't Radiographer ____
SNT-TC-1A Level ____
Reviewed By ____
SNT-TC-1A Level ____
Acceptance Code ____

Technique Used ____
T-1
T-2
T-3
Film
Source
Procedure Used ____

COMMENTS

Density Average ____
Area of Interest ____
Penetrameter ____
Differences ____

FIGURE 1. SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

B-6

WRITTEN BY	DATE	TECHNICAL REVIEW	DATE	COGNIZANT DIRECTOR	DATE	SS
[illegible]	7/[illegible]	[illegible]	7/82	Allen R. Whiting	7/82	CK

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

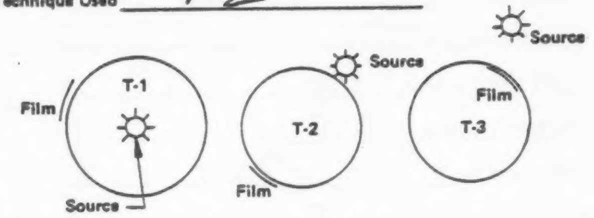
Page 1 of 1

System ______ Date 3-8-84
Sponsor DIV. III Project No. 03-7338-117 Date Rt. 3-7-84
Weld I.D. 002 Material CATALYST Cond. Pipe Size ______
Weld Thickness NA Shim NA Penetrameter NA FS/SS NA
Shooting: Single Wall ______ Double Wall ✓ Film Type KODAK M S/D S
Source Size ______ Curies ______ SFD ______ Time ______
X-Ray K.V. 140 M.A. 4 SFD 32" Time 5 1/2 min.
Film Evaluation: Reading: Single Film ✓ Double Film ______
One Wall on Film ______ Both Walls on Film ✓

Sketch Showing Setup

Radiographer OP Stiles
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By OP Stiles
SNT-TC-IA Level II

Technique Used T-2



NOTE: T-3 may also be used for plate

Applicable Code ______ Procedure Used OP 17-40-001

COMMENTS

Density Average ______
Area of Interest ______
Penetrameter ______
Difference ______

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through	
														.90 .50 .40 .36 .38 .50 .72 .72 AVE
														.5475
														.93 .83 .83 .75 .61 .67 .93 .98
														.8171
														AVE
														1.07 .69 .59 .63 .63 .65 .68 .99
														.7412
														105 119 1.10 .93 .84 .96 109 1 12
														1.0337

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page 1 of 1

System ____

Date 3-8-84

Sponsor DIV. III

Project No. 03-7338-117

Date Rt. 3-7-84

Weld I.D. 004

Material CATALYST CONV.

Pipe Size ____

Weld Thickness NA

Shim NA

Penetrameter NA

FS/SS NA

Shooting: Single Wall ____

Double Wall ✓

Film Type KODAK M

S/D 5

Source Size ____

Curies ____

SFD ____

Time ____

X-Ray K.V. 140

M.A. 4

SFD 32"

Time 7.0 MIN.

Film Evaluation: Reading: Single Film ✓

Double Film ____

One Wall on Film ____

Both Walls on Film ✓

Radiographer O.C. Stiles.

SNT-TC-IA Level II

Ass't Radiographer NA

SNT-TC-IA Level NA

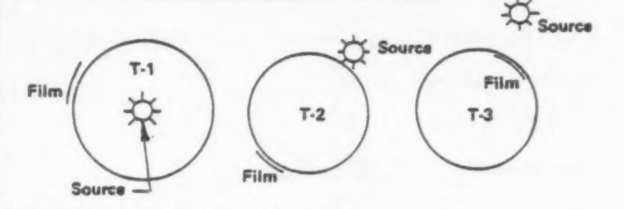
Reviewed By OC Stiles

SNT-TC-IA Level II

Applicable Code ____

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40001

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

COMMENTS

Density Average ____

Area of Interest ____

Penetrameter ____

Difference ____

Because of the added time needed for film exposure and film densities, this converter appears to have a heavier concentration of lead than the other converters.

This appearance could be because of a thicker housing or shell material.

AVE.

1.14 .78 .59 .49 .56 1.03

.7650

1.02 .81 .67 .63 .57 1.17

.8116

1.05 .90 .82 .81 .75 1.28

.9350

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page 1 of 1

System ________

Data 3-8-84

Sponsor DIV. III

Project No. 03-7338-117

Date Rt. 3-7-84

Weld I.D. 304-1

Material CATALYST CONV.

Pipe Size ________

Weld Thickness NA

Shim NA

Penetrameter NA

FS/SS NA

Shooting: Single Wall ________ Double Wall ✓

Film Type KODAK M

S/D 5

Source Size ________ Curies ________ SFD ________ Time ________

X-Ray K.V. 140

M.A. 4

SFD 32"

Time 5.5 min. FLAT 6.5 min. TILT

Film Evaluation: Reading: Single Film ✓ Double Film ________

One Wall on Film ________ Both Walls on Film —

Radiographer ________

SNT-TC-IA Level II

Ass't Radiographer NA

SNT-TC-IA Level NA

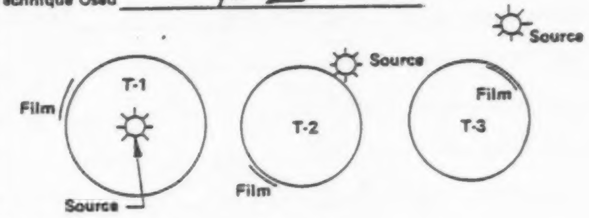
Reviewed By ________

SNT-TC-IA Level II

Applicable Code ________

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40-001

COMMENTS

Density Average ________

Area of Interest ________

Penetrameter ________

Difference ________

AVE

.93 .61 .51 .50 .47 .45 .47 .59

.5662

1.03 1.21 1.24 1.12 1.12 1.13 1.24 1.14

1.1537

AVE

.94 1.01 1.39 1.25 1.39 1.25 1.35 1.15

1.2162

1.10 1.38 1.61 1.39 1.35 1.32 1.27 1.08

1.3137

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page 1 of 1

System

Date 3-8-84

Sponsor DIV. III

Project No. 03-7338117

Weld I.D. 304-2

Material CATALYST CONN.

Date Rt. 3-7-84

Pipe Size

Weld Thickness NA

Shim NA

Penetrameter NA

FS/SS NA

Shooting: Single Wall

Double Wall ✓

Film Type KODAK M

S/D S

Source Size

Curies

SFD

Time

X-Ray K.V. 140

M.A. 4

SFD 32"

Time 5.5 MIN. FLAT 6.5 MIN. TILT

Film Evaluation: Reading: Single Film ✓

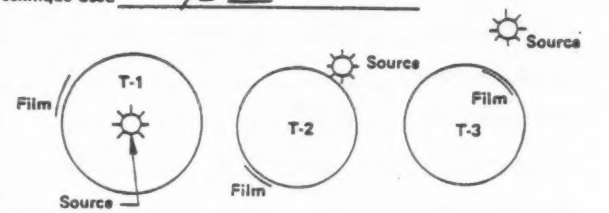
Double Film

One Wall on Film

Both Walls on Film ✓

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Radiographer

SNT-TC-IA Level II

Ass't Radiographer NA

SNT-TC-IA Level NA

Reviewed By

SNT-TC-IA Level II

Applicable Code

Procedure Used OP 17-40-001

COMMENTS

Density Average

Area of Interest

Penetrameter

Difference

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through	
														AVE
												B	6	1.22 1.30 1.25 1.27 ~~1.2~~ 1.32 1.39 1.32 1.09
														1.27
												B	5	1.23 1.35 1.23 1.25 1.27 1.19 1.01 1.10
														1.2037
												A	8	1.21 1.44 1.39 1.50 1.46 1.48 1.39 1.17
														1.380
												A	7	.70 .52 .50 .52 .61 .56 .66 .83
														.6125

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SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page 1 of 1

System ______ Date 3-8-84

Sponsor DIV. III Project No. 03-7338-117 Date Rt. 3-7-84

Weld I.D. 307 Material CATALYST CONV. Pipe Size ______

Weld Thickness NA Shim NA Penetrameter NA FS/SS NA

Shooting: Single Wall ______ Double Wall ______ Film Type KODAK M S/D S

Source Size ______ Curies ______ SFD ______ Time ______

X-Ray K.V. 140 M.A. 4 SFD 32" Time 5.5 min. FLAT 6.5 min. TILT

Film Evaluation: Reading: Single Film ______ Double Film ______

One Wall on Film ______ Both Walls on Film ______

Radiographer OC

SNT-TC-IA Level II

Ass't Radiographer NA

SNT-TC-IA Level NA

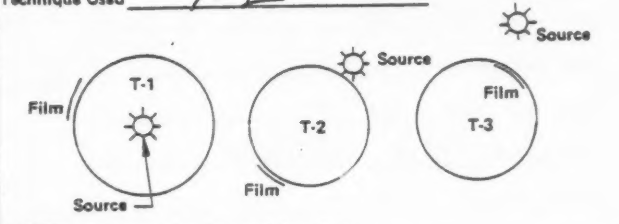
Reviewed By OP

SNT-TC-IA Level II

Applicable Code ______

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40-001

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

COMMENTS

Density Average ______

Area of Interest ______

Penetrameter ______

Difference ______

This side of honeycomb shows damage and possible crack.

AVE.

.102 .82 .68 .61 .67 .66 .73 .86

.7562

1.01 1.19 1.14 1.16 1.10 1.17 1.14 1.06

1.1212

This side of honeycomb shows damage and probable crack.

AVE

.94 1.07 1.04 1.03 1.25 1.14 1.03 .90

1.05

1.09 1.14 1.16 1.09 1.47 1.11 1.19 1.02

1.1597

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

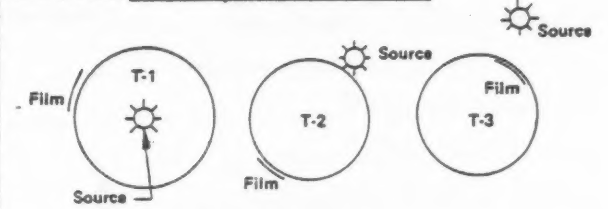
Page 1 of 1

System ______ Date 3-8-84
Sponsor DIV. III Project No. 03-7338-117 Date Rt. 3-7-84
Weld I.D. 309 Material CATALYST CONV. Pipe Size ______
Weld Thickness NA Shim NA Penetrameter NA FS/SS NA
Shooting: Single Wall ______ Double Wall ______ Film Type KODAK M S/D S
Source Size ______ Curies ______ SFD ______ Time ______
X-Ray K.V. 140 M.A. 4 SFD 32" Time 6.5 MIN. FLAT 7.5 MIN. TILT
Film Evaluation: Reading: Single Film ✓ Double Film ______
One Wall on Film ______ Both Walls on Film ✓

Radiographer O P
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By OP
SNT-TC-IA Level II
Applicable Code ______

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40-001

COMMENTS

Density Average ______
Area of Interest ______
Penetrameter ______
Difference ______

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through	AVE
												B	B	102 1.06 .95 .93 .91 .97 1.06 1.16
														1.0075
												B	F	.80 .69 .63 58 .60 .61 ,73 .90
														.6925
												A	B	.88 .98 .89 ,97 .96 .93 .92 ,80
														.9187
												A	F	1.01 1.04 .91 .89 83 .85 .88 .96
														.9212

Form SwRI NDT-RD-1, Rev. 1

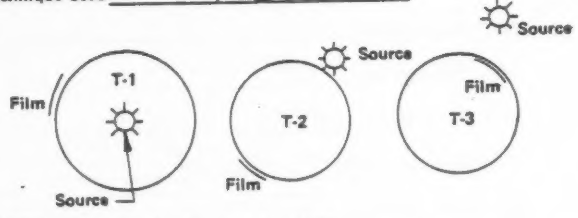
SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

Page 1 of 1

System ____
Date 3-8-84
Sponsor DIV. III
Project No 03-7338-117
Date Rt. 3-7-84
Weld I.D. 310-1
Material CATALYST CONV.
Pipe Size ____
Weld Thickness NA
Shim NA
Penetrameter NA
FS/SS NA
Shooting: Single Wall ____
Double Wall ✓
Film Type KODAK M
S/D S
Source Size ____
Curies ____
SFD ____
Time ____
X-Ray K.V. 140
M.A. 4
SFD 32"
Time 5.5 min FLAT 6.5 min TILT
Film Evaluation: Reading: Single Film ✓
Double Film ____
One Wall on Film ____
Both Walls on Film ✓

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Radiographer OC Stiles
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By OC Stiles
SNT-TC-IA Level II
Applicable Code ____
Procedure Used OP 17-40-001

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

COMMENTS

Density Average ____
Area of Interest ____
Penetrameter ____
Difference ____

AVE.

1.00 .90 .81 .80 .77 .89 .87 .92
.87

1.21 1.25 1.14 1.09 1.05 1.10 1.13 1.02
1.1237

1.24 1.37 1.49 1.52 1.48 1.29 1.40 1.40
1.3987

1.16 1.21 1.11 1.10 1.27 1.22 1.15 1.21
1.1787

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

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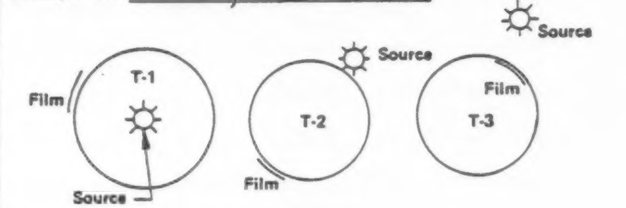
System ______ Date 3-8-84
Sponsor DIV. III Project No. 03-7338-117 Date Rt. 3-7-84
Weld I.D. 310-2 Material CATALYST PANV. Pipe Size ______
Weld Thickness NA Shim NA Penetrameter JA FS/SS NA
Shooting: Single Wall ______ Double Wall ✓ Film Type KODAK M S/D S
Source Size ______ Curies ______ SFD ______ Time ______
X-Ray K.V. 140 M.A. 4 SFD 32" Time 5.5 MIN. FLAT 6.5 MIN. TILT
Film Evaluation: Reading: Single Film ✓ Double Film ______
One Wall on Film ______ Both Walls on Film ✓

Radiographer OC
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By OC
SNT-TC-IA Level II
Applicable Code ______

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP-17-40-001

COMMENTS

Density Average ______
Area of Interest ______
Penetrameter ______
Difference ______

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through	
														AVE
												A		1.53 1.68 1.71 1.88 1.84 1.61 1.70 1.57
														1.69
												A		1.22 1.40 1.30 1.44 1.41 1.35 1.35 1.33
														1.3462
												A		1.22 1.28 1.48 1.27 1.38 1.42 1.32 1.17
														1.3175
												A		.94 .92 .82 .78 .76 .82 .89 1.02
														.86875

Form SwRI NDT-RD-1, Rev. 1

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

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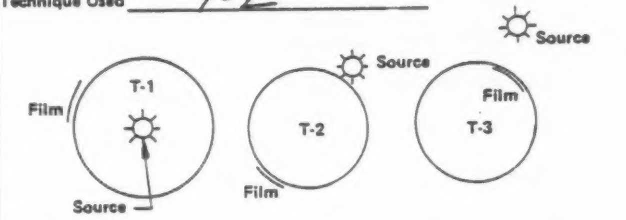
System ______ Date 3-8-84
Sponsor DIV. III Project No. 03-7338-117 Date Rt. 3-7-84
Weld I.D. 312 Material CATALYST MNK Pipe Size ______
Weld Thickness NA Shim NA Penetrameter NA FS/SS NA
Shooting: Single Wall ______ Double Wall ✓ Film Type KODAK M S/D S
Source Size ______ Curies ______ SFD ______ Time ______
X-Ray K.V. 140 M.A. 4 SFD 32" Time 5.5 MIN. FLAT 6.5 MIN TILT
Film Evaluation: Reading: Single Film ✓ Double Film ______
One Wall on Film ______ Both Walls on Film ✓

Sketch Showing Setup

Radiographer OC SDiles
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By OC SDiles
SNT-TC-IA Level II
Applicable Code ______

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40-001

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

COMMENTS

Density Average ______
Area of Interest ______
Penetrameter ______
Difference ______

This half of honey comb shows signs of damage with possible separation. AVE

1.07 .97 .87 .78 .84 1.03 .99 1.22

.965

1.11 1.36 1.42 1.35 1.40 1.44 1.33 1.19

1.325

This half of honey comb shows signs of damage to the point of a probable crack.

1.16 1.50 1.50 1.47 1.63 1.44 1.47 1.24

1.4262

1.12 1.49 1.52 1.57 1.67 1.41 1.35 1.20

1.415

SOUTHWEST RESEARCH INSTITUTE
RADIOGRAPHIC REVIEW RECORD

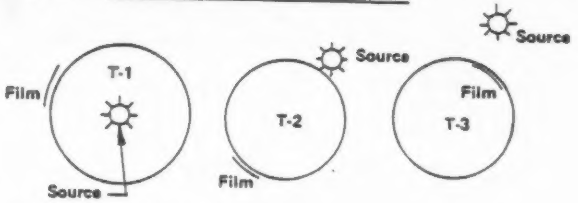
Page 1 of 1

System ______
Sponsor DIV. III
Project No. 03-7338-117
Date 3-8-84
Weld I.D. 9H
Material CATALYST CONT.
Date Rt. 3-7-84
Weld Thickness NA
Pipe Size ______
Shim NA
Penetrameter NA
FS/SS NA
Shooting: Single Wall ______
Double Wall ______
Film Type KODAK M
S/D S
Source Size ______
Curies ______
SFD ______
Time ______
X-Ray K.V. 140
M.A. 4
SFD 32"
Time 5.6 MIN FLAT 6.5 MIN. TILT
Film Evaluation: Reading: Single Film ✓
Double Film ______
One Wall on Film ______
Both Walls on Film ✓

Radiographer O. C. Stiles
SNT-TC-IA Level II
Ass't Radiographer NA
SNT-TC-IA Level NA
Reviewed By O C Stiles
SNT-TC-IA Level II
Applicable Code ______

Sketch Showing Setup

Technique Used T-2



NOTE: T-3 may also be used for plate

Procedure Used OP 17-40-001

Film Ident.	Accept	Reject	Porosity	Linear Indication	Slag	Overgrind	Crater Crack	Crack(s)	Tungsten	L.O.F.	L.O.P.	Undercut (ID-OD)	Burn Through

COMMENTS

Density Average ______
Area of Interest ______
Penetrameter ______
Difference ______

AVE

.89 .69 .57 .53 .50 .56 .61 .70

.6312

1.00 1.22 1.18 1.05 1.11 1.20 1.18 1.06

1.125

1.11 1.24 1.38 1.40 1.36 1.28 1.38 1.23

1.2975

1.04 1.38 1.35 1.31 1.19 1.20 1.33 1.26

1.2575

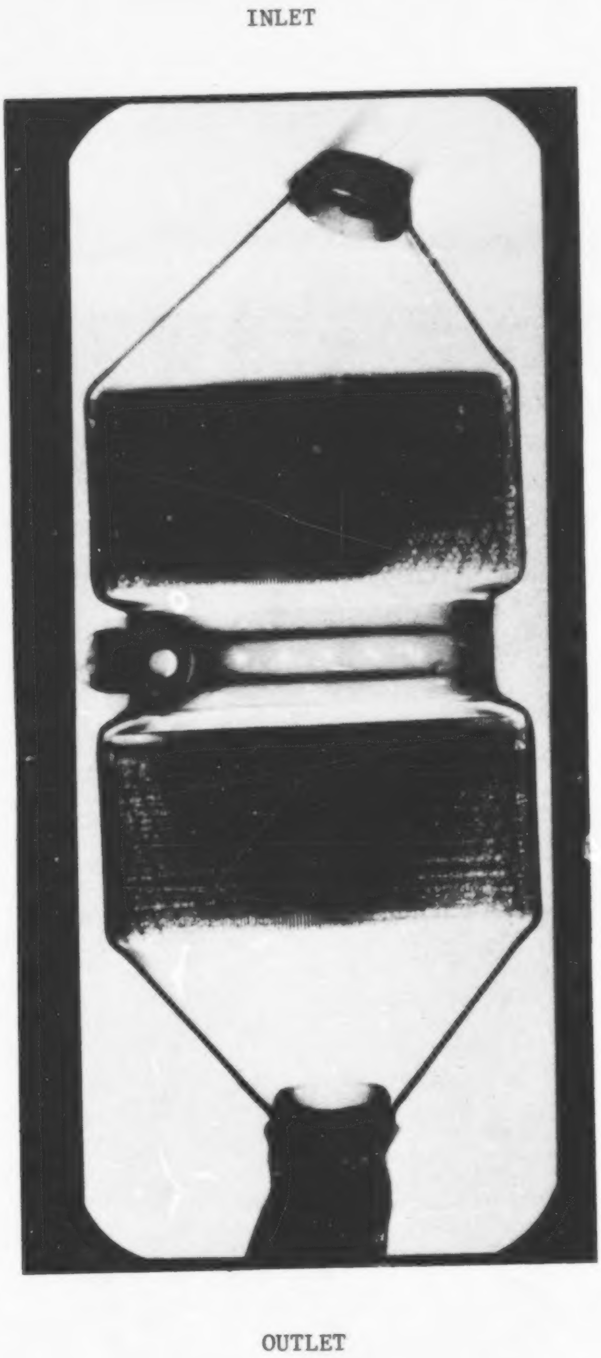
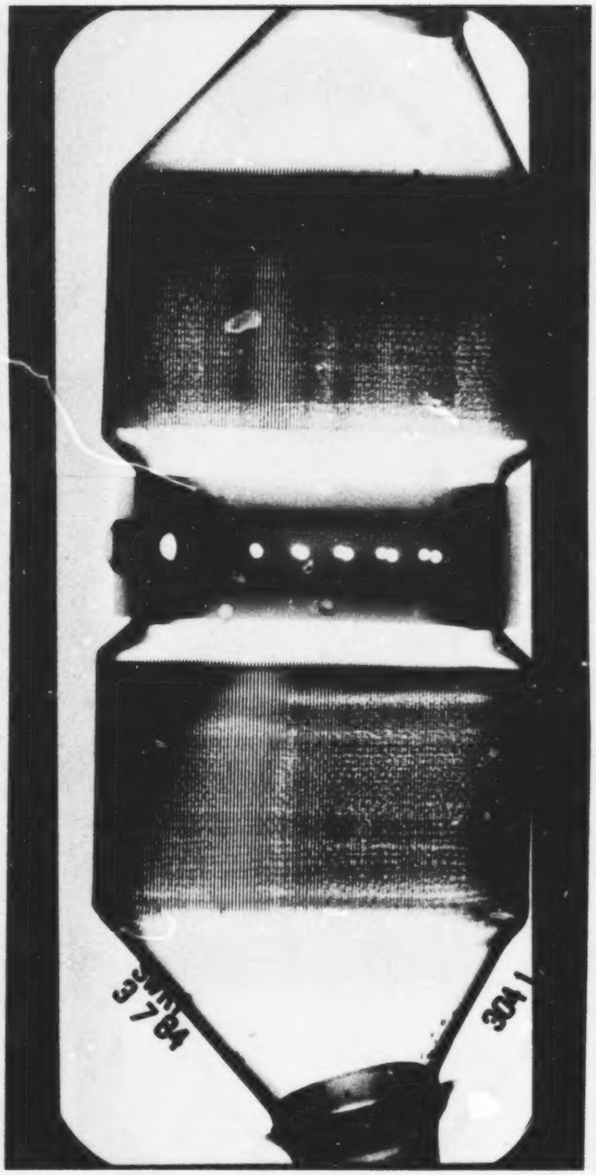

INLET
OUTLET

Figure B-1. Whole catalyst x-ray of 002

INLET
OUTLET

Figure B-2. Whole Catalyst x-ray of 004

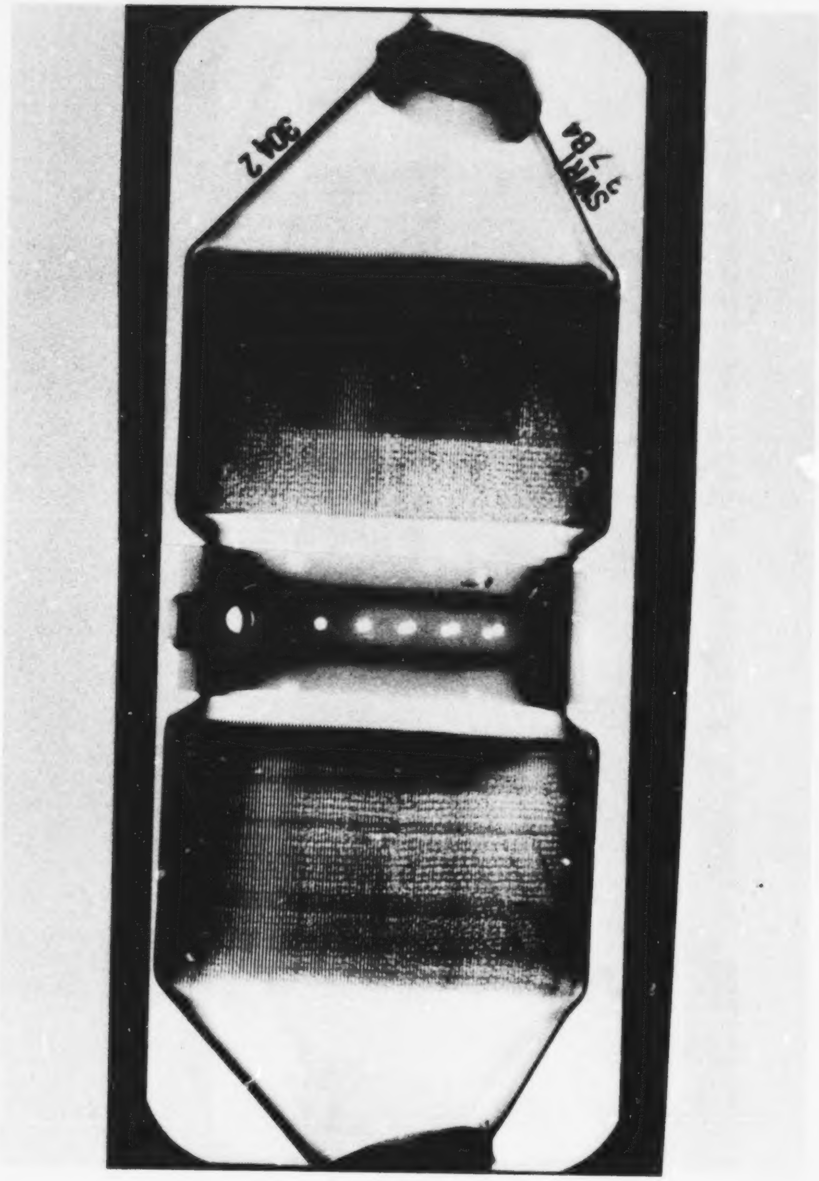
INLET



OUTLET

Figure B-3. Whole catalyst x-ray of 304-1

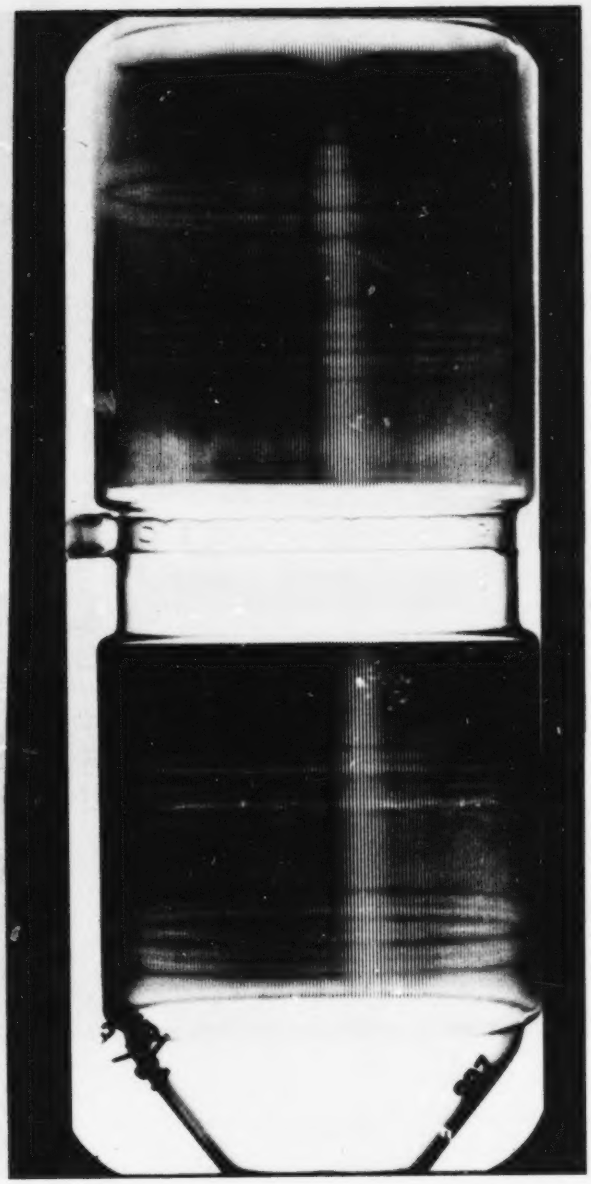
INLET


304 2
SWRI 3 784

OUTLET

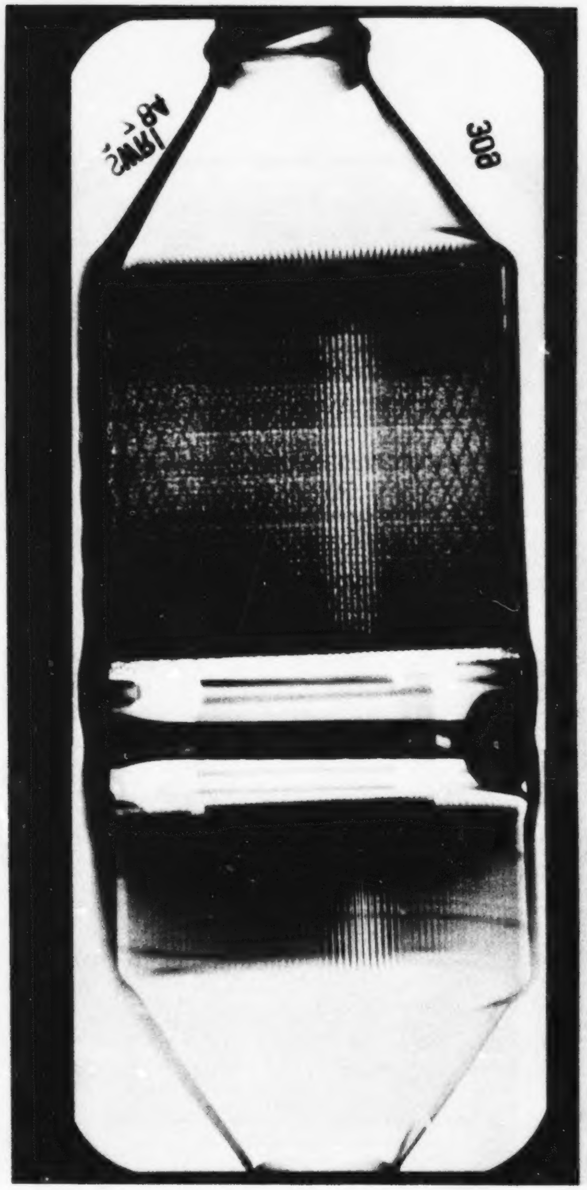
Figure B-4. Whole catalyst x-ray of 304-2

INLET



OUTLET

Figure B-5. Whole catalyst x-ray of 307

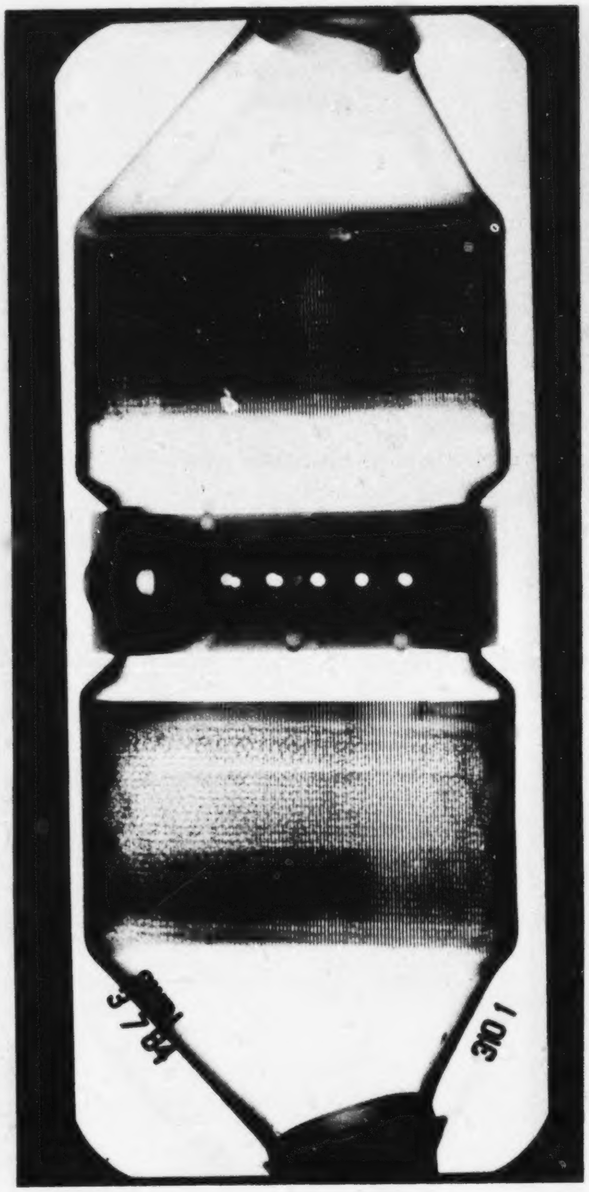


INLET

OUTLET

Figure B-6. Whole catalyst x-ray of 309

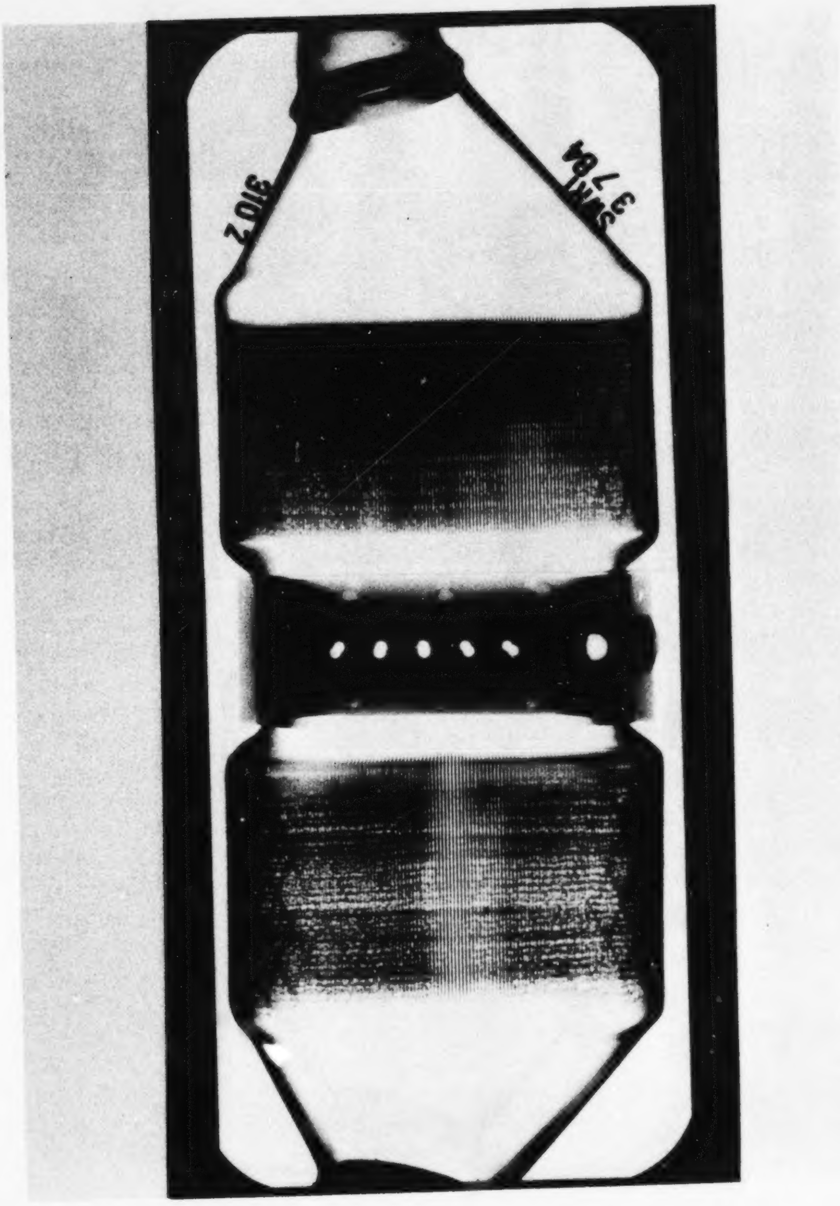
INLET



OUTLET

Figure B-7. Whole catalyst x-ray of 310-1

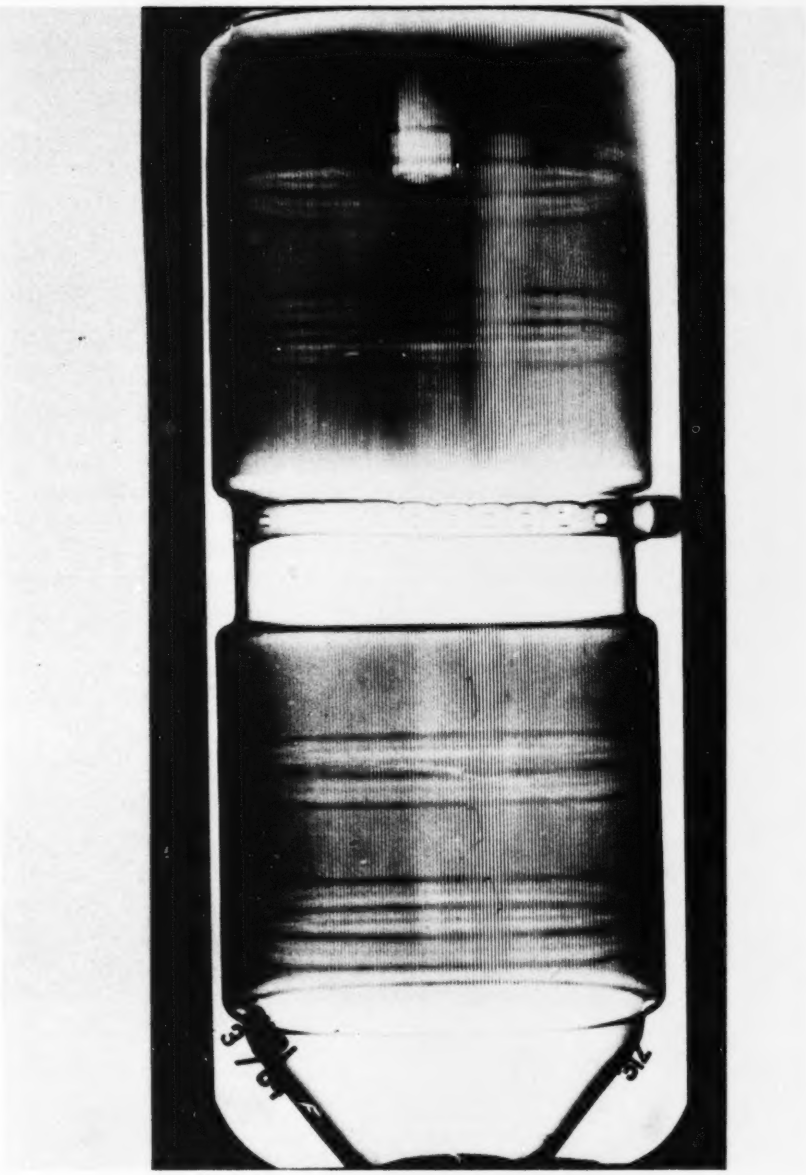
INLET



OUTLET

Figure B-8. Whole catalyst x-ray of 310-2

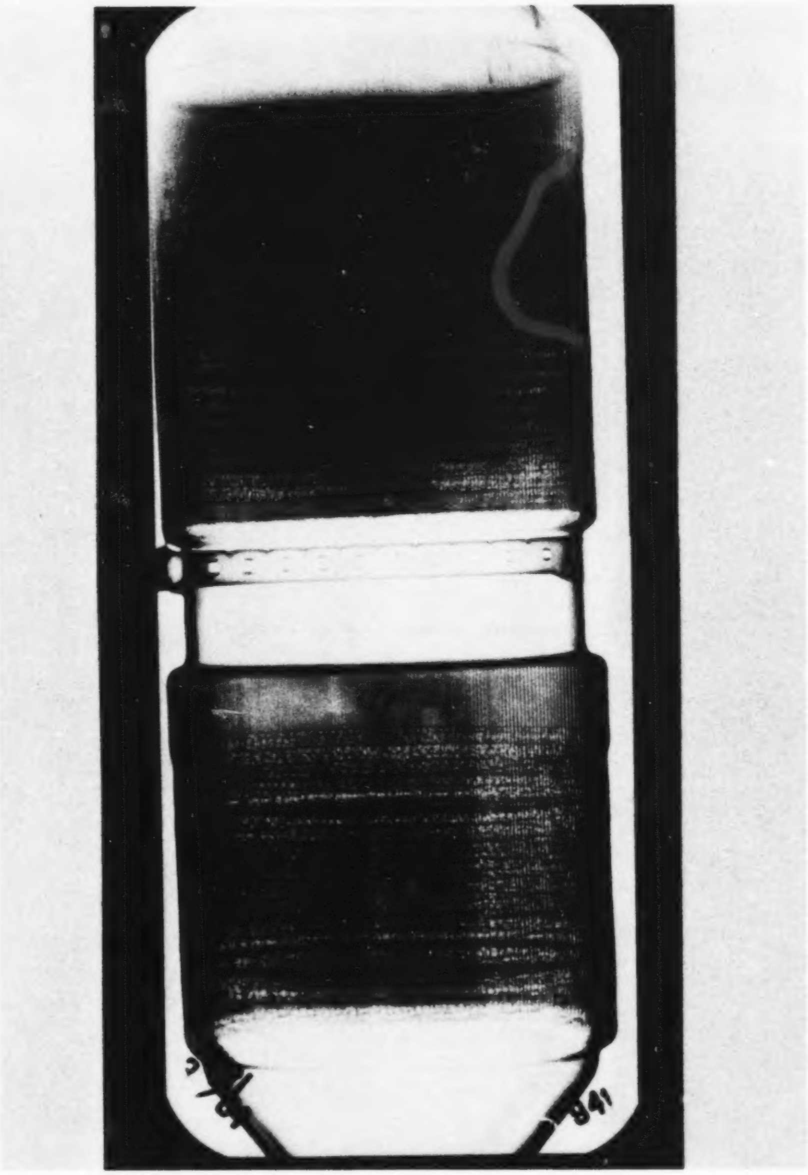
INLET



OUTLET

Figure B-9. Whole catalyst x-ray of 312

INLET



OUTLET

Figure B-10. Whole catalyst x-ray of 941

APPENDIX C

SURFACE AREA BY BET ANALYSIS

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                                                     NITROGEN
OUTHWEST RSCH, 002-A, MAL# 850-46
TATION 1          STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 12:12

                          ADSORPTION ISOTHERM

                                       EQUILIBRATION INTERVAL:     20 SECS
AMPLE WEIGHT:      5.1550 G            MAX VOL INCREMENT:   100.000 CC/G STP
REE SPACE:       151.5430 CC

                  P/PO                 VOL ADSORBED
                                       (CC/G AT STP)

                 0.0547                   2.0690
                 0.0799                   2.2045
                 0.1196                   2.3799
                 0.1597                   2.5363
                 0.2000                   2.6822
```

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                     MERITICS INSTRUMENT CORPORATION

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                                                     NITROGEN
SOUTHWEST RSCH, 002-A, MAL# 850-46
STATION 1         STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 12:12

                        SPECIFIC SURFACE AREA

           BET SURFACE AREA:           9.6385   +/-    0.0188 SQ M/G
           SLOPE:                      0.448156 +/-    0.000874
           INTERCEPT:                  0.003489 +/-    0.000117
           C:                        129.4422
           VM:                         2.2141 CC


           RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                  MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 002-B, MAL# 851-47                          NITROGEN
STATION 2         STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 12:59

                         ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.0780 G            EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       150.8245 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                     P/PO               VOL ADSORBED
                                        (CC/G AT STP)

                     0.0526                0.9657
                     0.0789                1.0310
                     0.1200                1.1083
                     0.1599                1.1757
                     0.2001                1.2371


                  MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 002-B, MAL# 851-47                          NITROGEN
STATION 2         STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 12:59

                        SPECIFIC SURFACE AREA

        BET SURFACE AREA:           4.4178   +/-     0.0165 SQ M/G
        SLOPE:                      0.979649 +/-     0.003652
        INTERCEPT:                  0.005736 +/-     0.000487
        C:                        171.7993
        VM:                         1.0148 CC


        RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                 MERITICS INSTRUMENT CORPORATION

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SOUTHWEST RESEARCH 004 MAL #882-44                         NITROGEN
STATION 2          STARTED  4/10/84 10:48    COMPLETED  4/10/84 15: 9

                       ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.8440 G            EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       152.5417 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                 P/PO                   VOL ADSORBED
                                        (CC/G AT STP)

                 0.0546                    1.2965
                 0.0800                    1.3786
                 0.1198                    1.4831
                 0.1598                    1.5793
                 0.1999                    1.6703


             MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RESEARCH 004 MAL #882-44                         NITROGEN
STATION 2          STARTED  4/10/84 10:48    COMPLETED  4/10/84 15: 9

                      SPECIFIC SURFACE AREA

           BET SURFACE AREA:            5.9878   +/-    0.0092 SQ M/G
           SLOPE:                       0.721781 +/-    0.001113
           INTERCEPT:                   0.005234 +/-    0.000149
           C:                         138.8938
           VM:                          1.3755 CC


           RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                 MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 304-1-A, MAL# 852-48                       NITROGEN
STATION 3          STARTED  4/ 4/84  8:30   COMPLETED  4/ 4/84 13:57

                       ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.7710 G           EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       154.0035 CC          MAX VOL INCREMENT:   100.000 CC/G STP

                 P/PO                  VOL ADSORBED
                                       (CC/G AT STP)

                 0.0523                   2.2188
                 0.0776                   2.3682
                 0.1198                   2.5578
                 0.1595                   2.7208
                 0.2001                   2.8751


                 MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 304-1-A, MAL# 852-48                       NITROGEN
STATION 3          STARTED  4/ 4/84  8:30   COMPLETED  4/ 4/84 13:57

                      SPECIFIC SURFACE AREA

          BET SURFACE AREA:           10.2955    +/-    0.0165 SQ M/G
          SLOPE:                       0.419912 +/-    0.000673
          INTERCEPT:                   0.002914 +/-    0.000090
          C:                         145.0908
          VM:                          2.3650 CC


          RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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SOUTHWEST RSCH, 304-1-B, MAL# 853-254                             NITROGEN
STATION 4          STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 14:59

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.9110 G               EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       154.2870 CC              MAX VOL INCREMENT:   100.000 CC/G STP

                   P/PO                    VOL ADSORBED
                                           (CC/G AT STP)

                   0.0533                      2.9311
                   0.0769                      3.1168
                   0.1197                      3.3766
                   0.1597                      3.5957
                   0.2000                      3.8036


                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 304-1-B, MAL# 853-254                             NITROGEN
STATION 4          STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 14:59

                         SPECIFIC SURFACE AREA

          BET SURFACE AREA:              13.6433  +/-     0.0177 SQ M/G
          SLOPE:                          0.316734 +/-    0.000411
          INTERCEPT:                      0.002338 +/-    0.000055
          C:                            136.4876
          VM:                             3.1341 CC


          RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                                                          NITROGEN
SOUTHWEST RSCH, 304-2-A, MAL# 854-255
STATION 5          STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 16: 5

                          ADSORPTION ISOTHERM

                                         EQUILIBRATION INTERVAL:    20 SECS
SAMPLE WEIGHT:      4.3520 G             MAX VOL INCREMENT:   100.000 CC/G STP
FREE SPACE:       155.6340 CC

                   P/PO                  VOL ADSORBED
                                         (CC/G AT STP)

                   0.0546                   2.6971
                   0.0798                   2.9805
                   0.1195                   3.1158
                   0.1597                   3.3261
                   0.1996                   3.5340
```

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                                                          NITROGEN
SOUTHWEST RSCH, 304-2-A, MAL# 854-255
STATION 5          STARTED  4/ 4/84  8:30    COMPLETED  4/ 4/84 16: 5

                          SPECIFIC SURFACE AREA

               BET SURFACE AREA:          12.7364   +/-    0.0274 SQ M/G
               SLOPE:                      0.338786 +/-    0.000729
               INTERCEPT:                  0.003005 +/-    0.000097
               C:                        113.7332
               VM:                         2.9258 CC


               RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 304-2-B, MAL# 855-2-B                             NITROGEN
STATION 1           STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 20:54

                            ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.0740 G           EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       130.8320 CC          MAX VOL INCREMENT:   100.000 CC/G STP

                      P/PO             VOL ADSORBED
                                       (CC/G AT STP)

                     0.0523               0.9576
                     0.0786               1.0243
                     0.1199               1.1015
                     0.1598               1.1717
                     0.2000               1.2338


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SOUTHWEST RSCH. 304-2-B, MAL# 855-2-B                             NITROGEN
STATION 1           STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 20:54

                           SPECIFIC SURFACE AREA

          BET SURFACE AREA:              4.4144   +/-    0.0148 SQ M/G
          SLOPE:                         0.979898 +/-    0.003282
          INTERCEPT:                     0.006248 +/-    0.000438
          C:                           157.8297
          VM:                            1.0140 CC


          RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 307-A, MAL# 866-44                          NITROGEN
STATION 4        STARTED  4/ 5/84 16:26    COMPLETED  4/ 6/84  6: 8

                           ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.9430 G           EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       154.1124 CC          MAX VOL INCREMENT:   100.000 CC/G STP

                    P/PO               VOL ADSORBED
                                       (CC/G AT STP)

                    0.0543                 4.8073
                    0.0800                 5.1556
                    0.1182                 5.5845
                    0.1595                 5.9652
                    0.1998                 6.3316


                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 307-A, MAL# 866-44                          NITROGEN
STATION 4        STARTED  4/ 5/84 16:26    COMPLETED  4/ 6/84  6: 8

                          SPECIFIC SURFACE AREA

            BET SURFACE AREA:           22.8584  +/-    0.0314 SQ M/G
            SLOPE:                      0.188712 +/-    0.000260
            INTERCEPT:                  0.001730 +/-    0.000035
            C:                        110.1055
            VM:                         5.2310 CC


            RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                 MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 307-B, MAL# 867-46                           NITROGEN
STATION 1          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 15:37

                        ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.3840 G          EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       152.1426 CC         MAX VOL INCREMENT:   100.000 CC/G STP

                  P/PO                VOL ADSORBED
                                      (CC/G AT STP)

                  0.0502                 4.0119
                  0.0799                 4.3202
                  0.1192                 4.6810
                  0.1595                 5.0094
                  0.2002                 5.3077


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SOUTHWEST RSCH, 307-B, MAL# 867-46                           NITROGEN
STATION 1          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 15:37

                        SPECIFIC SURFACE AREA

            BET SURFACE AREA:        19.1663   +/-    0.0448 SQ M/G
            SLOPE:                    0.225066 +/-    0.000526
            INTERCEPT:                0.002063 +/-    0.000070
            C:                      110.1095
            VM:                       4.4028 CC


            RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
```

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                  MICROMERITICS INSTRUMENT CORPORATION

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                                                             NITROGEN
SOUTHWEST RSCH, 308-A, MAL# 868-47
STATION 2          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 16:32

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.8500 G            EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       151.0779 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                  P/PO                  VOL ADSORBED
                                        (CC/G AT STP)

                 0.0540                    1.6573
                 0.0783                    1.7618
                 0.1198                    1.9020
                 0.1598                    2.0249
                 0.2002                    2.1358
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                       MERITICS INSTRUMENT CORPORATION

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                                                             NITROGEN
SOUTHWEST RSCH, 308-A, MAL# 868-47
STATION 2          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 16:32

                        SPECIFIC SURFACE AREA

           BET SURFACE AREA:             7.6527   +/-    0.0213 SQ M/G
           SLOPE:                        0.564935 +/-    0.001571
           INTERCEPT:                    0.003909 +/-    0.000210
           C:                          145.5101
           VM:                           1.7580 CC


           RELATIVE PRESSURE RANGE: 0.0300 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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                                                            NITROGEN
SOUTHWEST RSCH, 309-B, MAL# 869-48
STATION 3          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 17:29

                          ADSORPTION ISOTHERM

                                        EQUILIBRATION INTERVAL:    20 SECS
SAMPLE WEIGHT:      4.6380 G
FREE SPACE:       154.4223 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                   P/PO                 VOL ADSORBED
                                        (CC/G AT STP)

                   0.0548                  1.1639
                   0.0799                  1.2417
                   0.1197                  1.3355
                   0.1594                  1.4244
                   0.1996                  1.4997
```

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                    MICROMERITICS INSTRUMENT CORPORATION

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                                                            NITROGEN
SOUTHWEST RSCH, 309-B, MAL# 869-48
STATION 3          STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 17:29

                         SPECIFIC SURFACE AREA

           BET SURFACE AREA:          5.3861   +/-     0.0219 SQ M/G
           SLOPE:                     0.802473 +/-     0.003262
           INTERCEPT:                 0.005751 +/-     0.000435
           C:                       140.5249
           VM:                        1.2373 CC


           RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-1-A, MAL# 880-265                          NITROGEN
STATION 2           STARTED  4/11/84 15:33    COMPLETED  4/11/84 20:57

                          SPECIFIC SURFACE AREA

             BET SURFACE AREA:              18.1776   +/-     0.0448 SQ M/G
             SLOPE:                          0.237619 +/-     0.000585
             INTERCEPT:                      0.001863 +/-     0.000078
             C:                            128.5383
             VM:                             4.1757 CC


             RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-1-A, MAL# 880-265                          NITROGEN
STATION 2           STARTED  4/11/84 15:33    COMPLETED  4/11/84 20:57

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.0910 G         EQUILIBRATION INTERVAL:     20 SECS
FREE SPACE:       154.3802 CC        MAX VOL INCREMENT:   100.000 CC/G STP

                 P/PO                VOL ADSORBED
                                     (CC/G AT STP)

                 0.0533                  3.8766
                 0.0799                  4.1557
                 0.1193                  4.4860
                 0.1595                  4.7831
                 0.2001                  5.0564
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-1-B, MAL# 879-264                      NITROGEN
STATION 1          STARTED  4/11/84 15:33    COMPLETED  4/11/84 19:37

                           ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.0350 G             EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       151.6677 CC            MAX VOL INCREMENT:   100.000 CC/G STP

                    P/PO                 VOL ADSORBED
                                         (CC/G AT STP)

                    0.0536                  3.7117
                    0.0800                  3.9809
                    0.1194                  4.3012
                    0.1597                  4.5873
                    0.2002                  4.8538
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-1-B, MAL# 879-264                      NITROGEN
STATION 1          STARTED  4/11/84 15:33    COMPLETED  4/11/84 19:37

                         SPECIFIC SURFACE AREA

              BET SURFACE AREA:           17.4618   +/-    0.0362 SQ M/G
              SLOPE:                       0.247286 +/-    0.000512
              INTERCEPT:                   0.002013 +/-    0.000068
              C:                         123.8594
              VM:                          4.0113 CC


              RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-2-A, MAL# 878-256                       NITROGEN
STATION 5          STARTED  4/ 9/84  8: 6    COMPLETED  4/10/84  4:35

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.1780 G               EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       153.5794 CC              MAX VOL INCREMENT:   100.000 CC/G STP

                P/PO                       VOL ADSORBED
                                           (CC/G AT STP)

                0.0543                        3.4327
                0.0787                        3.6593
                0.1195                        3.9623
                0.1597                        4.2238
                0.2003                        4.4666
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-2-A, MAL# 878-256                       NITROGEN
STATION 5          STARTED  4/ 9/84  8: 6    COMPLETED  4/10/84  4:35

                         SPECIFIC SURFACE AREA


           BET SURFACE AREA:          16.0555  +/-     0.0356 SQ M/G
           SLOPE:                      0.269010 +/-    0.000595
           INTERCEPT:                  0.002125 +/-    0.000079
           C:                        127.5810
           VM:                         3.6882 CC



           RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                 MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-2-B, MAL# 881-266                        NITROGEN
STATION 3           STARTED  4/11/84 15:33    COMPLETED  4/11/84 22:10

                        ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.0740 G           EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       153.4321 CC          MAX VOL INCREMENT:  100.000 CC/G STP

                   P/PO                VOL ADSORBED
                                       (CC/G AT STP)

                  0.0544                   3.4430
                  0.0785                   3.6662
                  0.1195                   3.9699
                  0.1597                   4.2306
                  0.2002                   4.4716
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                 MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 310-2-B, MAL# 881-266                        NITROGEN
STATION 3           STARTED  4/11/84 15:33    COMPLETED  4/11/84 22:10

                       SPECIFIC SURFACE AREA

          BET SURFACE AREA:            16.0666   +/-    0.0373 SQ M/G
          SLOPE:                        0.268865 +/-    0.000623
          INTERCEPT:                    0.002083 +/-    0.000083
          C:                          130.1035
          VM:                           3.6908 CC


          RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                   MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 312-A, MAL# 870-250                           NITROGEN
STATION 4           STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 18:25

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      4.5500 G            EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       153.1110 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                      P/PO              VOL ADSORBED
                                        (CC/G AT STP)

                     0.0548                0.3385
                     0.0795                0.3630
                     0.1198                0.3894
                     0.1598                0.4108
                     0.1998                0.4269


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                                  101

SOUTHWEST RSCH, 312-A, MAL# 870-250                           NITROGEN
STATION 4           STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 18:25

                         SPECIFIC SURFACE AREA

            BET SURFACE AREA:              1.5235   +/-    0.0198 SQ M/G
            SLOPE:                         2.845330 +/-    0.036838
            INTERCEPT:                     0.012130 +/-    0.004921
            C:                           235.5601
            VM:                            0.3500 CC


            RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 312-B, MAL# 871-255                                NITROGEN
STATION 5            STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 19:19

                         ADSORPTION ISOTHERM

SAMPLE WEIGHT:       0.1020 G              EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:        152.0577 CC             MAX VOL INCREMENT:   100.000 CC/G STP

                  P/PO                     VOL ADSORBED
                                           (CC/G AT STP)

                 0.0548                       1.1781
                 0.0787                       1.2587
                 0.1198                       1.3595
                 0.1568                       1.4527
                 0.1989                       1.5334


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SOUTHWEST RSCH, 312-B, MAL# 871-255                                NITROGEN
STATION 5            STARTED  4/ 6/84 11:53    COMPLETED  4/ 6/84 19:19

                        SPECIFIC SURFACE AREA

          BET SURFACE AREA:            5.5199   +/-    0.0175 SQ M/G
          SLOPE:                       0.782325 +/-    0.002483
          INTERCEPT:                   0.006307 +/-    0.000332
          C:                         125.0492
          VM:                          1.2680 CC


          RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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                    MICROMERITICS INSTRUMENT CORPORATION

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SOUTHWEST RSCH, 041-A,  MAL# 856-265                              NITROGEN
STATION 2         STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 22: 9

                          ADSORPTION ISOTHERM

SAMPLE WEIGHT:      0.1880 G           EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       153.0381 CC          MAX VOL INCREMENT:   100.000 CC/G STP

                     P/PO              VOL ADSORBED
                                       (CC/G AT STP)

                     0.0535               3.9917
                     0.0798               4.1736
                     0.1191               4.5141
                     0.1594               4.8244
                     0.2000               5.1109


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                          DIGISORB 2600 V2.02                          PAGE  2
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SOUTHWEST RSCH, 041-A,  MAL# 856-265                              NITROGEN
STATION 2         STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 22: 9

                         SPECIFIC SURFACE AREA

            BET SURFACE AREA:           18.4213    +/-     0.0382 SQ M/G
            SLOPE:                       0.234284  +/-     0.000486
            INTERCEPT:                   0.002030  +/-     0.000065
            C:                         116.4289
            VM:                          4.2317 CC


            RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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SOUTHWEST RSCH, 341-B, MAL# 857-266                            NITROGEN
STATION C             STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 23:35

                            ADSORPTION ISOTHERM

SAMPLE WEIGHT:      5.1250 G            EQUILIBRATION INTERVAL:    20 SECS
FREE SPACE:       152.4400 CC           MAX VOL INCREMENT:   100.000 CC/G STP

                    P/PO                VOL ADSORBED
                                        (CC/G AT STP)

                   0.0547                  5.0967
                   0.0796                  5.4496
                   0.1166                  5.8996
                   0.1585                  6.3072
                   0.2003                  6.6795


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                            DIGISORB 2600 V2.02                        PAGE  2
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SOUTHWEST RSCH, 341-B, MAL# 857-266                            NITROGEN
STATION C             STARTED  4/ 4/84 17:47    COMPLETED  4/ 4/84 23:35

                          SPECIFIC SURFACE AREA

           BET SURFACE AREA:          24.0838   +/-    0.0561 SQ M/G
           SLOPE:                      0.179184 +/-    0.000417
           INTERCEPT:                  0.001568 +/-    0.000056
           C:                        115.2632
           VM:                         5.5324 CC


           RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100
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Liquid Chromatography Instruments/Particle Technology Instruments

April 11, 1984

Mr. Robert E. Fanick
Southwest Research Institute
6220 Culebra
San Antonio, Texas 78284

Reference: Your Purchase Order #29318
Micromeritics' File #110723-044-MSP
Your Purchase Order #30660
Micromeritics' File #110605-034-MSP

Dear Mr. Fanick:

The Materials Analysis Laboratory has analyzed your samples on our Digi-Sorb 2600. Enclosed are data sheets of the results.

Summary of the results:

Sample Identification	Specific Surface Area (m^2/g)
Monolith Catalyst P.O. #29318	
#1 312-A	1.5
#2 312-B	5.5
#3 307-A	22.9
#4 307-B	19.2
#5 309-A	7.7
#6 309-B	5.4
P.O. #30660	
#1 941-A	18.4
#2 941-B	24.1
#3 002-A	9.6
#4 002-B	4.4
#5 304-1-A	10.3
#6 304-1-B	13.6
#7 304-2-A	12.7
#8 304-2-B	4.4

If you have questions, or if we can better serve you, please contact us.

Sincerely,

Pat McCann, Manager
Materials Analysis Laboratory

Represented by:
Richard Geary
6907 Leandra Drive
Houston, Texas 77083

MICROMERITICS INSTRUMENT CORPORATION
5680 Goshen Springs Road • Norcross, Georgia 30093 USA Telephone (404) 448-8282 • International Telex: 682 7018

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Liquid Chromatography Instruments/Particle Technology Instruments

April 17, 1984

Mr. Robert F. Fanick
Southwest Research Institute
6220 Culebra
San Antonio, TX 78284

Reference: Your Purchase Order #30664
Micromeritics' File #110722-044-MSP

Dear Mr. Fanick:

The Materials Analysis Laboratory has analyzed your samples on our Digi-Sorb 2600. Enclosed are data sheets of the results.

Summary of the results:

Sample Identification	Specific Surface Area (m^2/g)
Monolith Catalyst	
310-1-A	18.2
310-1-B	17.5
310-2-A	16.1
310-2-B	16.1
004	6.0

If you have questions, or if we can better serve you, please contact us.

Sincerely,

Pat McCann, Manager
Materials Analysis Laboratory

Represented by:
Richard Geary
6907 Leandra Drive
Houston, TX 77083
(713) 784-1148

P.S. Completing the enclosed Sample Submission Form will simplify our procedures and will result in decreasing the overall turnaround time of your samples. We appreciate your returning the completed form with your samples.

APPENDIX D

ELEMENTAL ANALYSIS BY X-RAY FLUORESCENCE

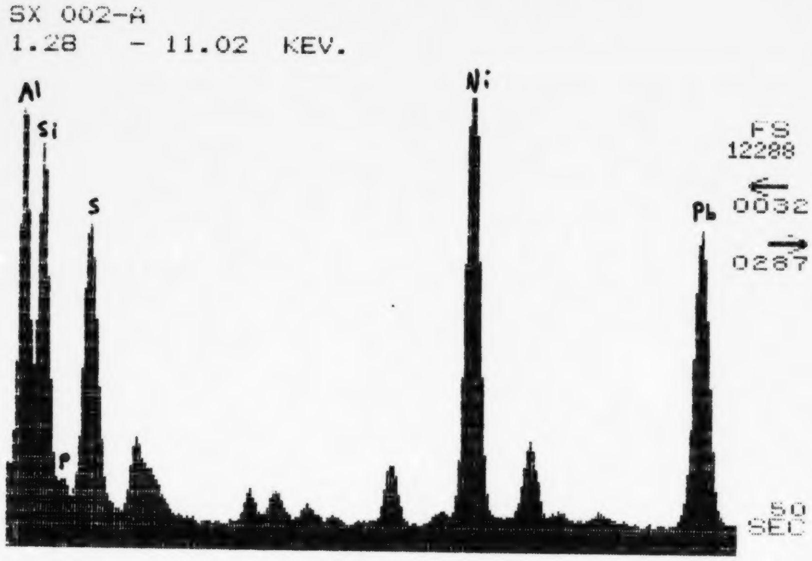

Figure D-1. Elemental analysis of catalyst 002-A

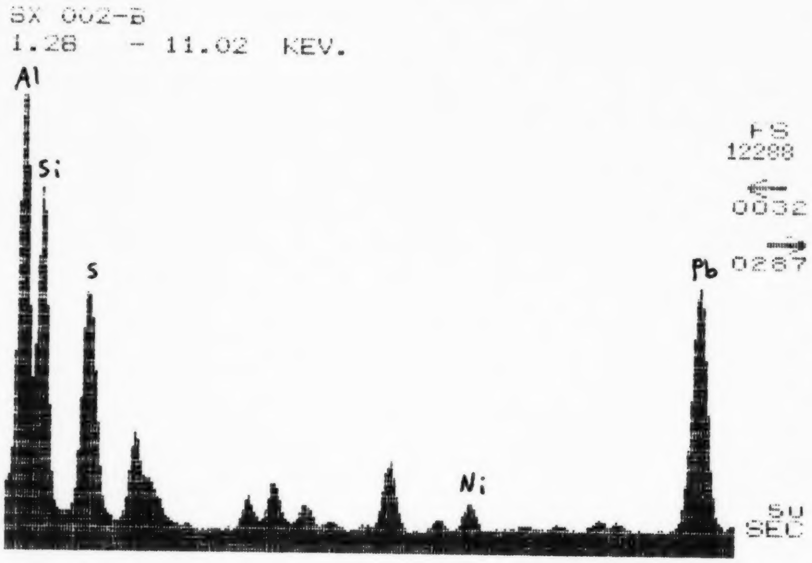

Figure D-2. Elemental analysis of catalyst 002-B

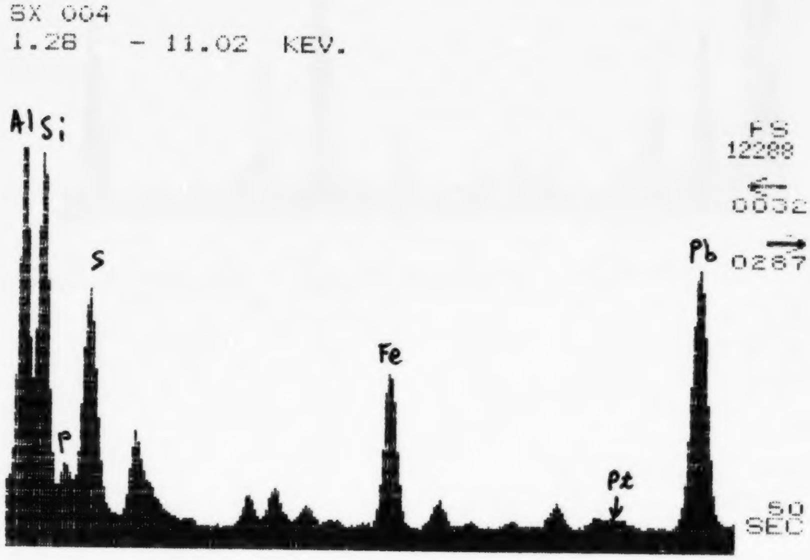

Figure D-3. Elemental analysis of catalyst 004

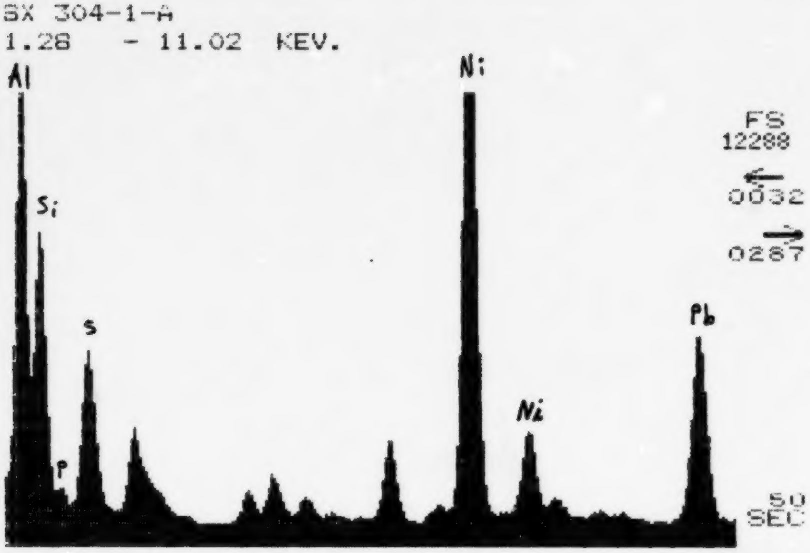

Figure D-4. Elemental analysis of catalyst 304-1-A

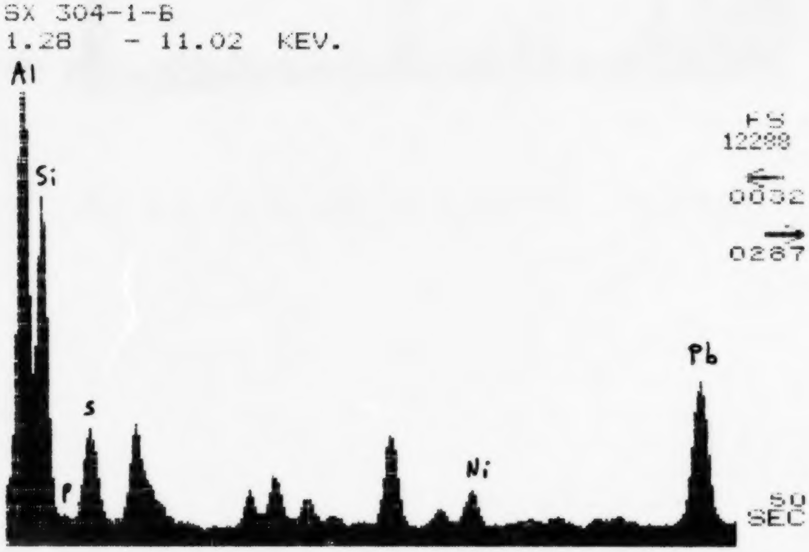

Figure D-5. Elemental analysis of catalyst 304-1-B

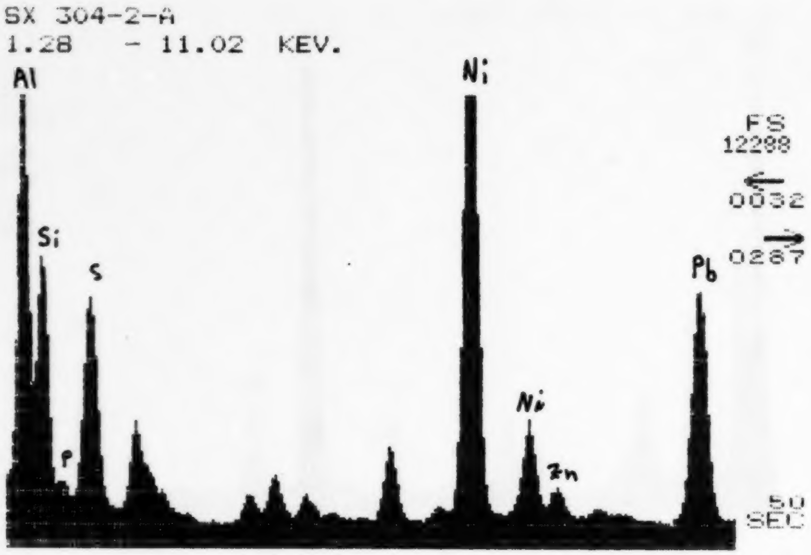

Figure D-6. Elemental analysis of catalyst 304-2-A

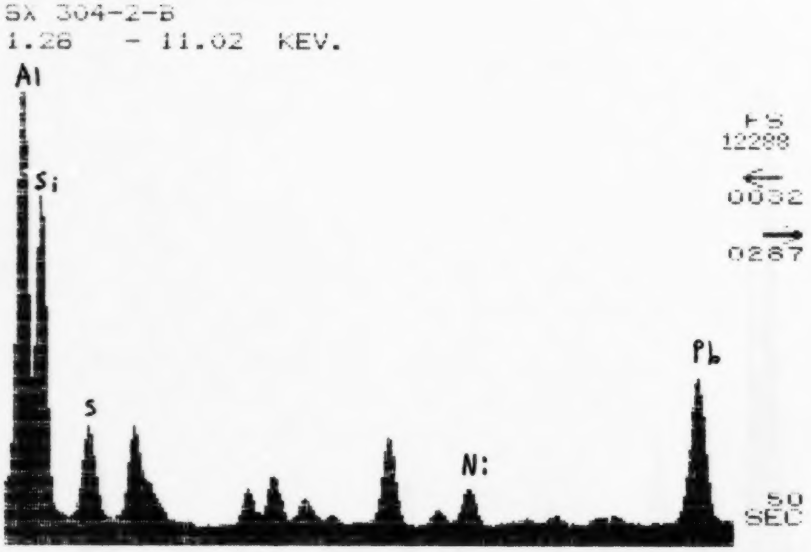

Figure D-7. Elemental analysis of catalyst 304-2-B

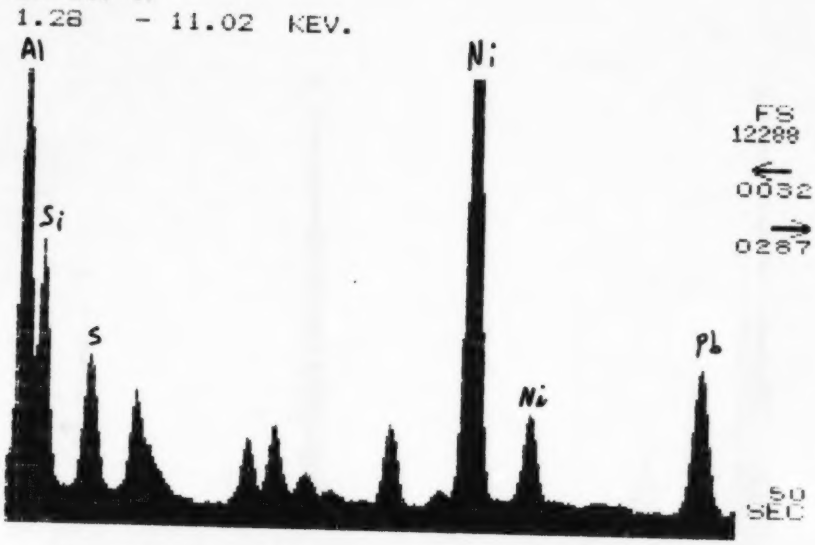

Figure D-8. Elemental analysis of catalyst 307-A

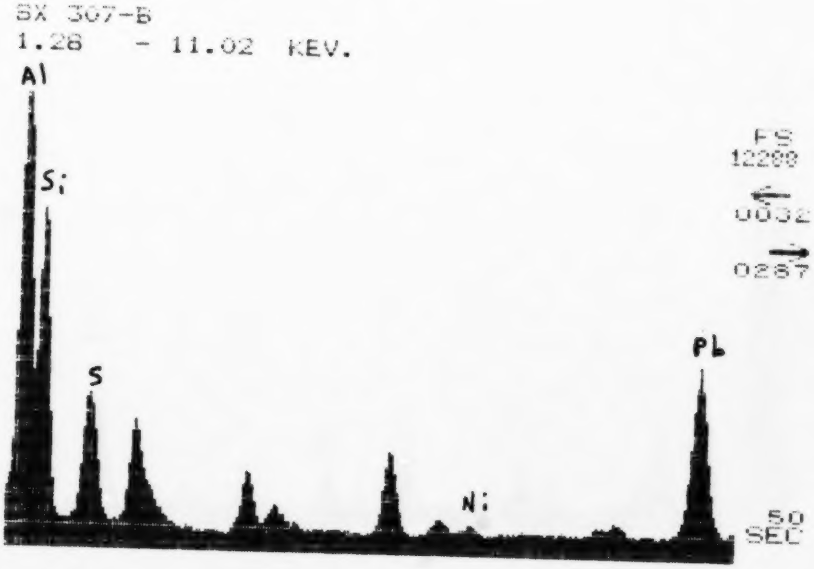

Figure D-9. Elemental analysis of catalyst 307-B

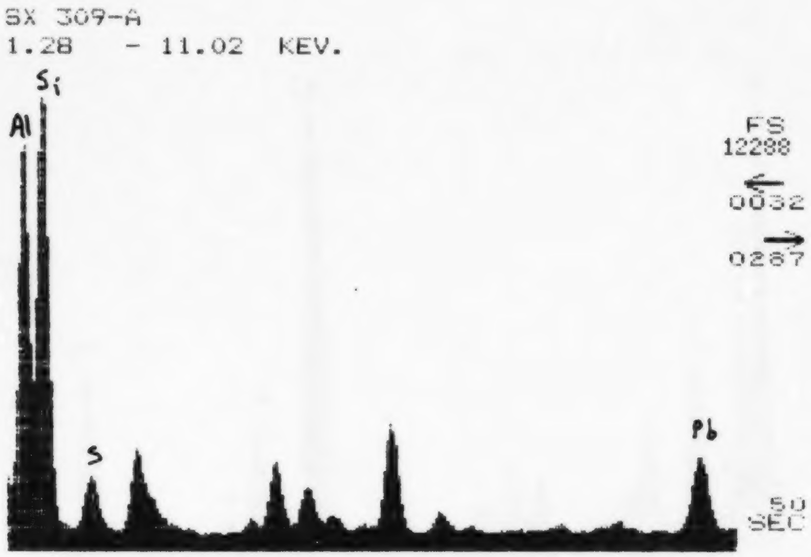

Figure D-10. Elemental analysis of catalyst 309-A

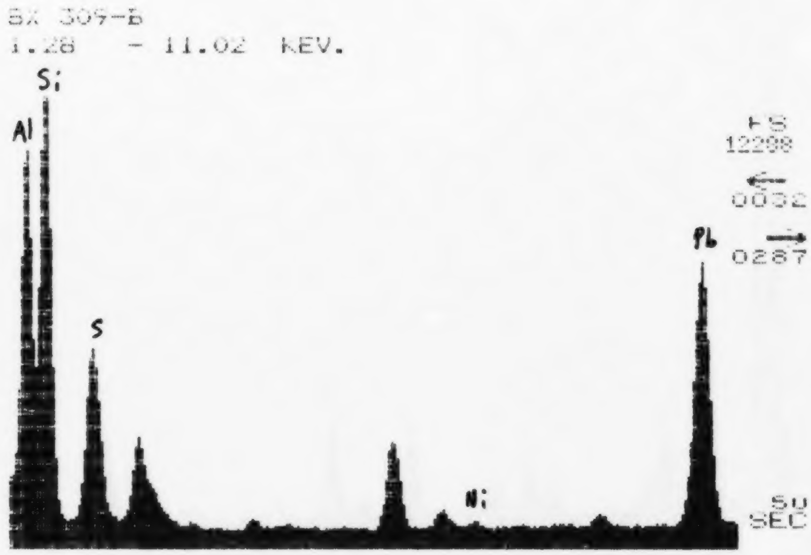

Figure D-11. Elemental analysis of catalyst 309-B

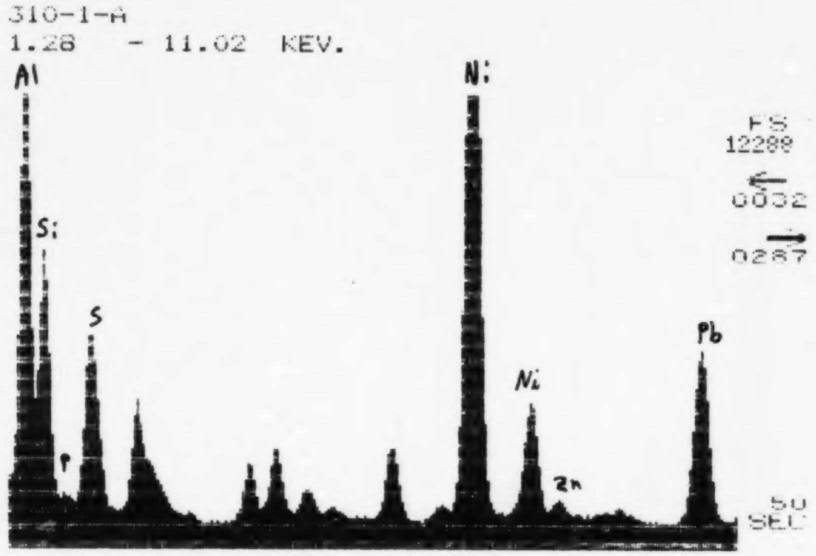

Figure D-12. Elemental analysis of catalyst 310-1-A

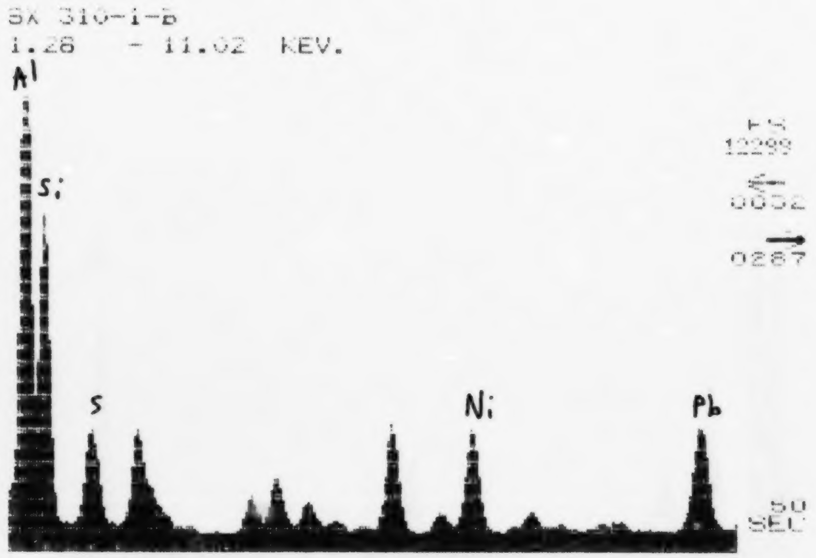

Figure D-13. Elemental analysis of catalyst 310-1-B

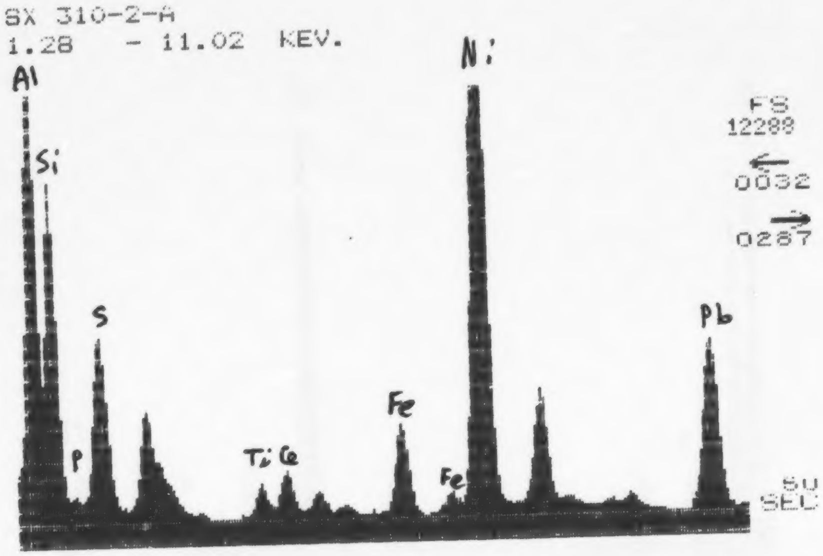

Figure D-14. Elemental analysis of catalyst 310-2-A

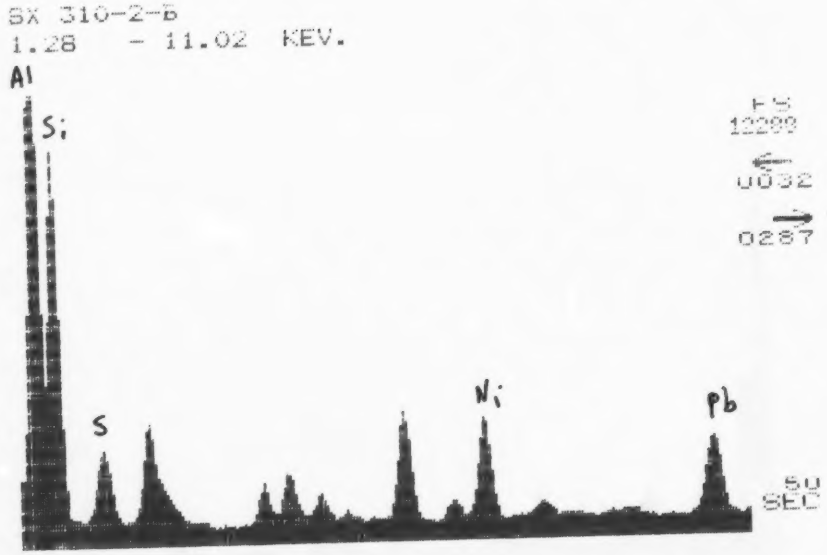

Figure D-15. Elemental analysis of catalyst 310-2-B

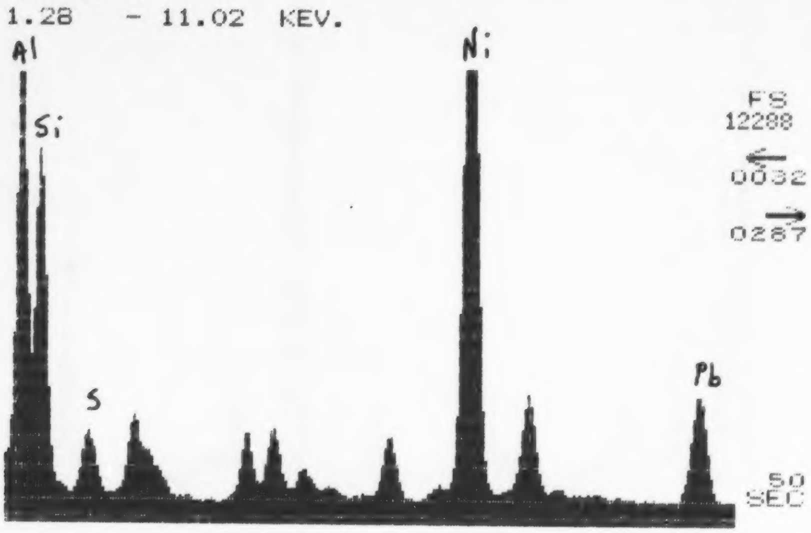

Figure D-16. Elemental analysis of catalyst 312-A

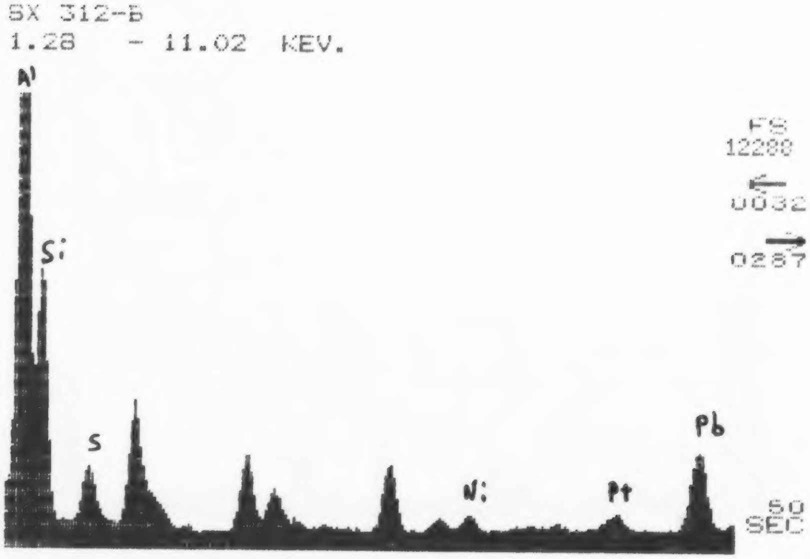

Figure D-17. Elemental analysis of catalyst 312-B

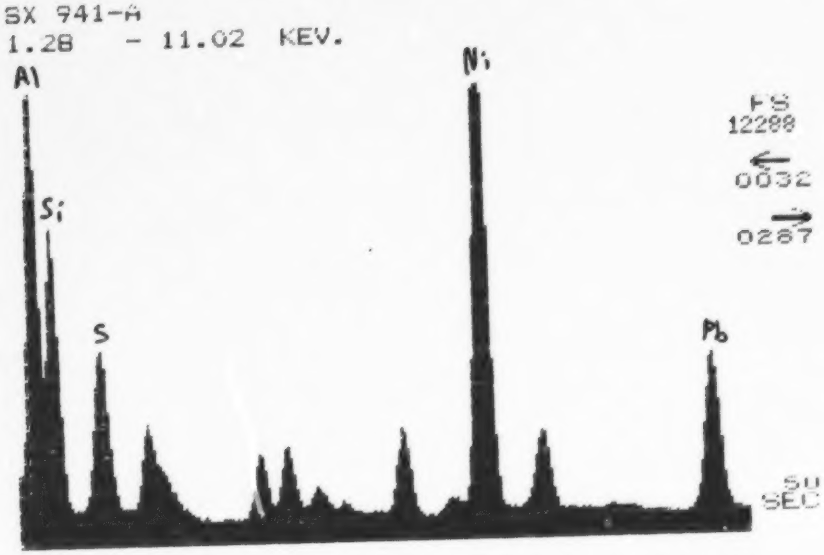

Figure D-18. Elemental analysis of catalyst 941-A

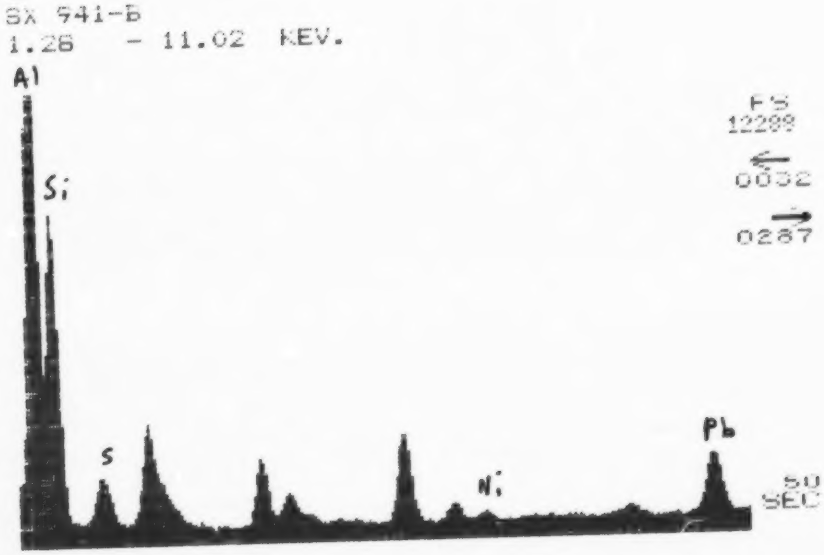

Figure D-19. Elemental analysis of catalyst 941-B

APPENDIX E

MICROGRAPHS FROM SCANNING ELECTRON MICROSCOPE

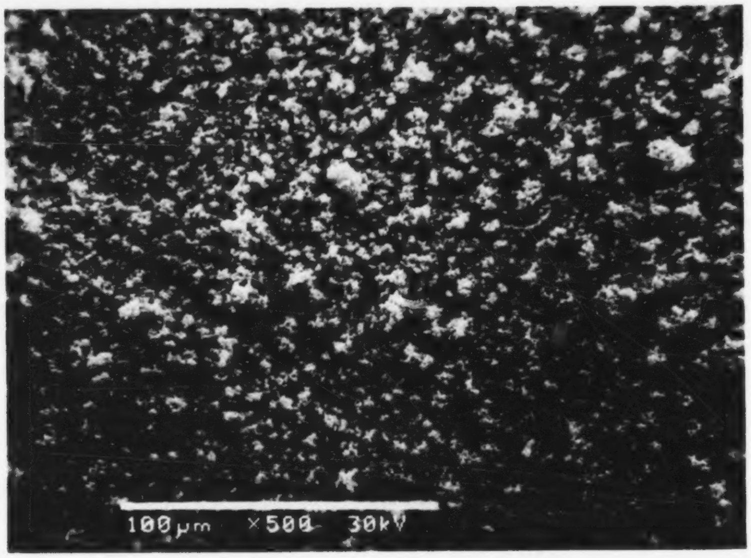
100µm ×500 30kV

Figure E-1. Micrograph of 002-A (500X)

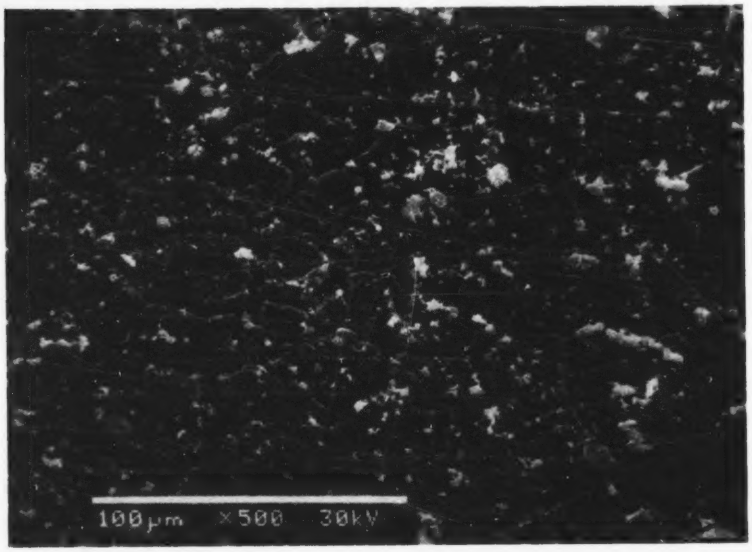
100µm ×500 30kV

Figure E-2. Microgrpah of 002-B (500X)

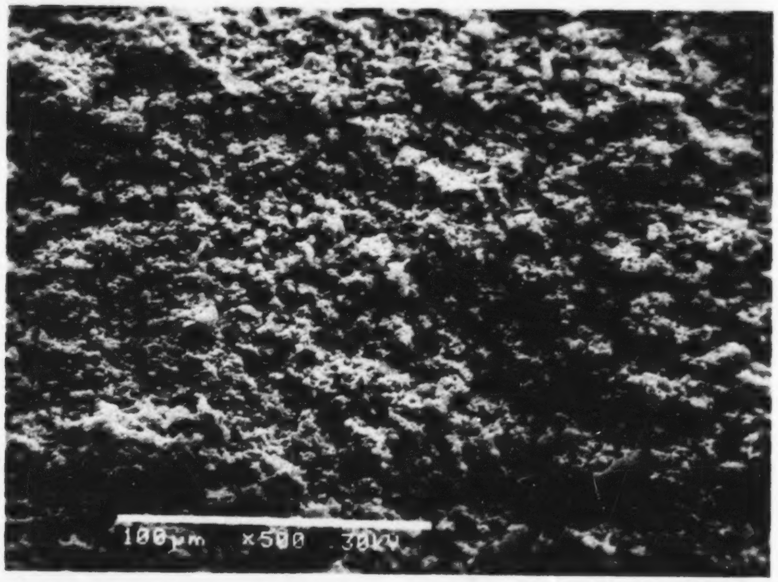
100μm ×500 30kV

Figure E-3. Micrograph of 004 (500X)

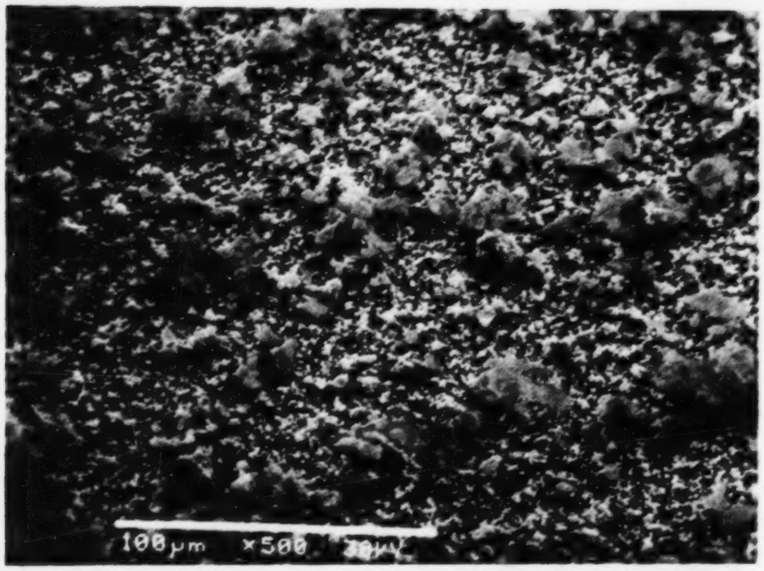
100μm ×500 30kV

Figure E-4. Micrograph of 304-1-A (500X)

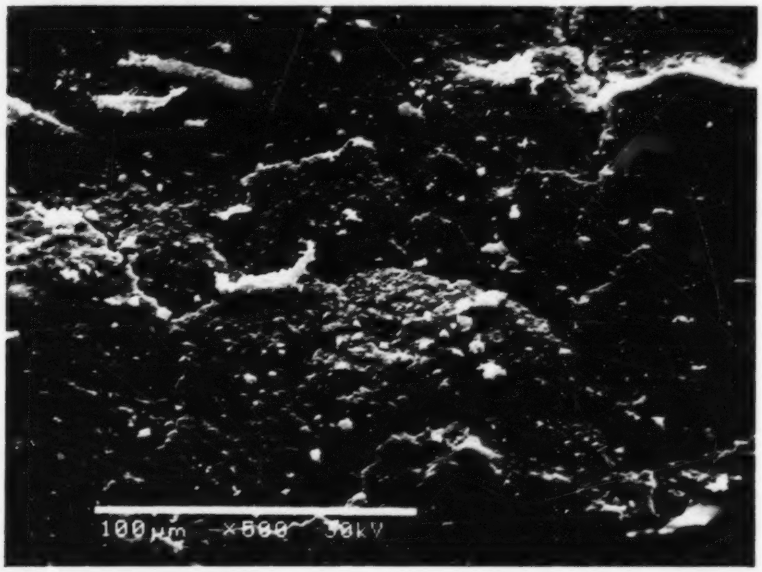
100μm ×500 30kV

Figure E-5. Micrograph of 304-1B (500X)

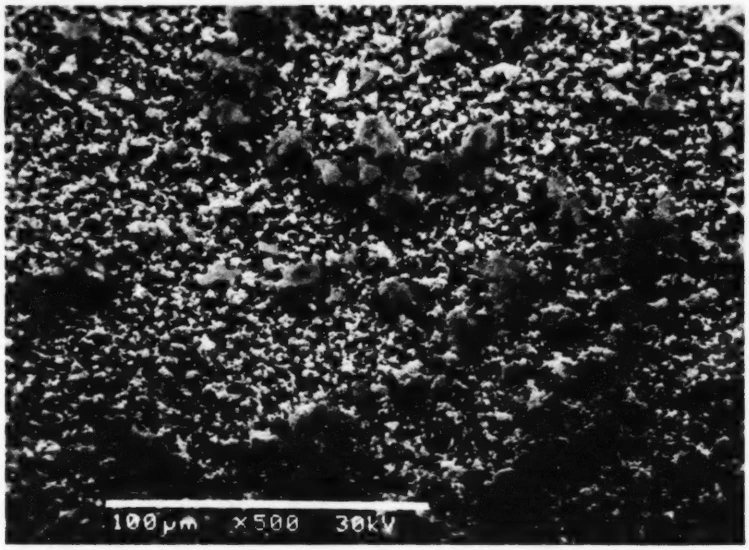
100μm ×500 30kV

Figure E-6. Micrograph of 304-2-A (500X)

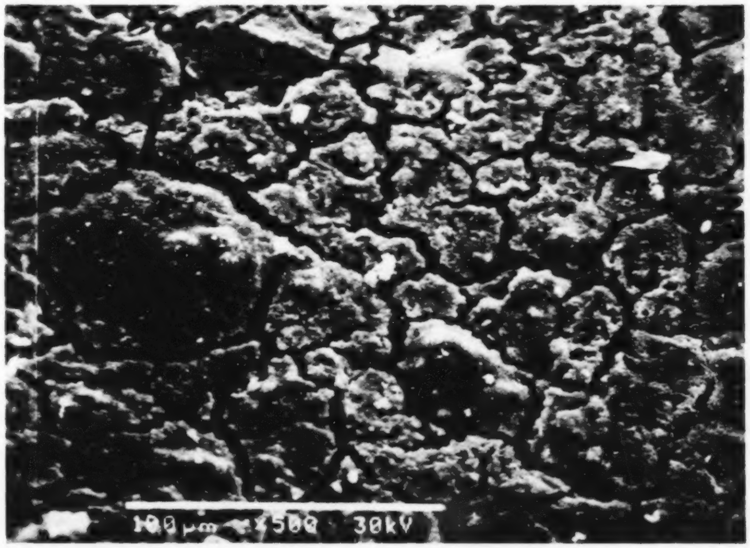
100μm ×500 30kV

Figure E-7. Micrograph of 304-2-B (500X)

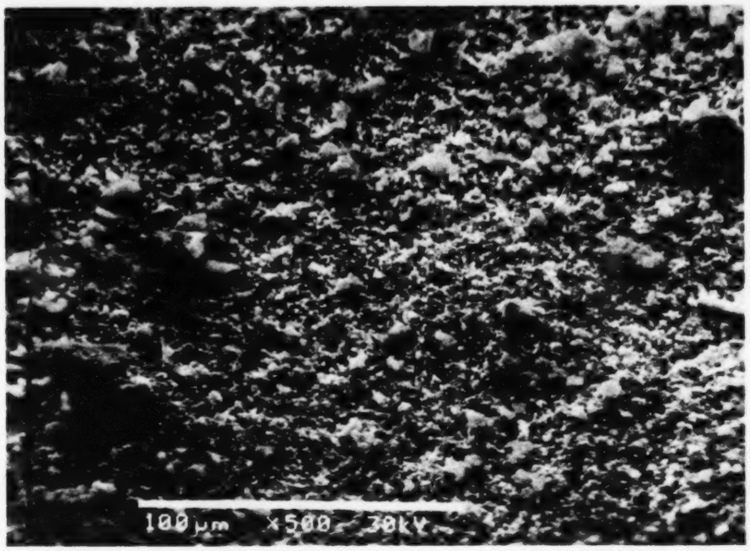
100μm ×500 30kV

Figure E-8. Micrograph of 307-A (500X)

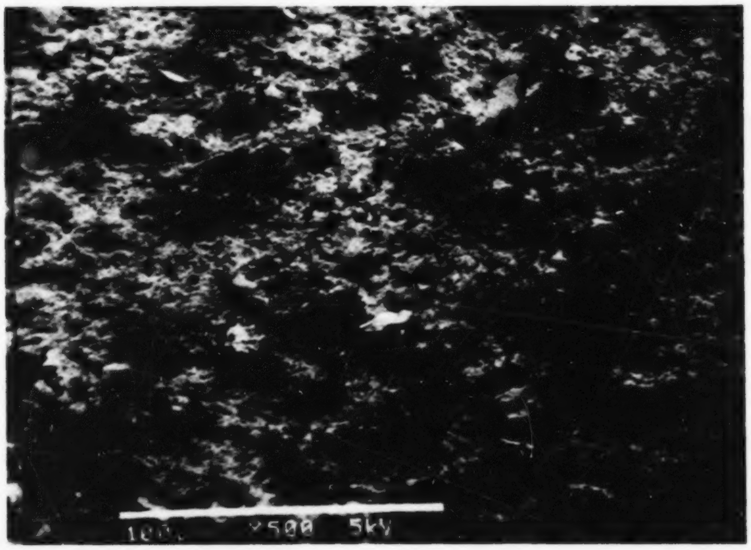

Figure E-9. Micrograph of 307-B (500X)

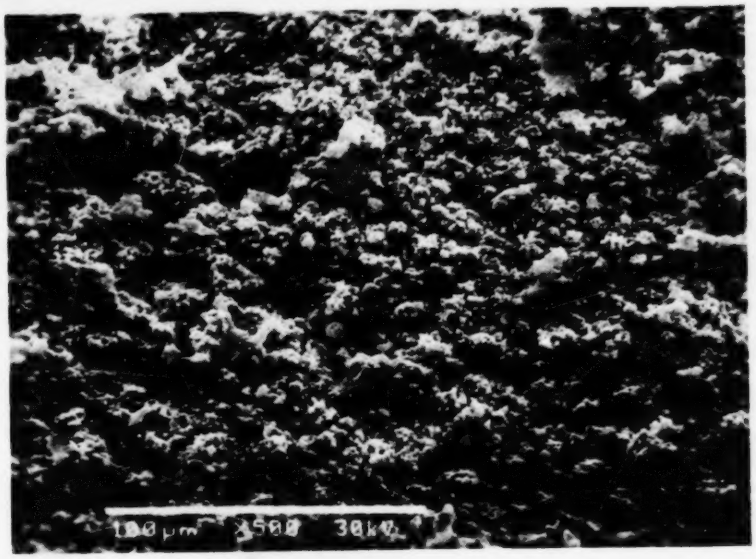
100μm X500 30kV

Figure E-10. Micrograph of 309-A (500X)

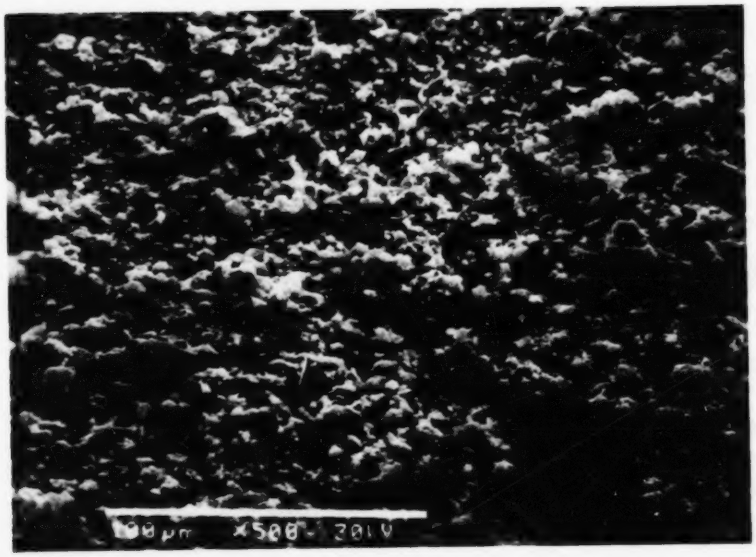
100μm X500 30kV

Figure E-11. Micrograph of 309-B (500X)

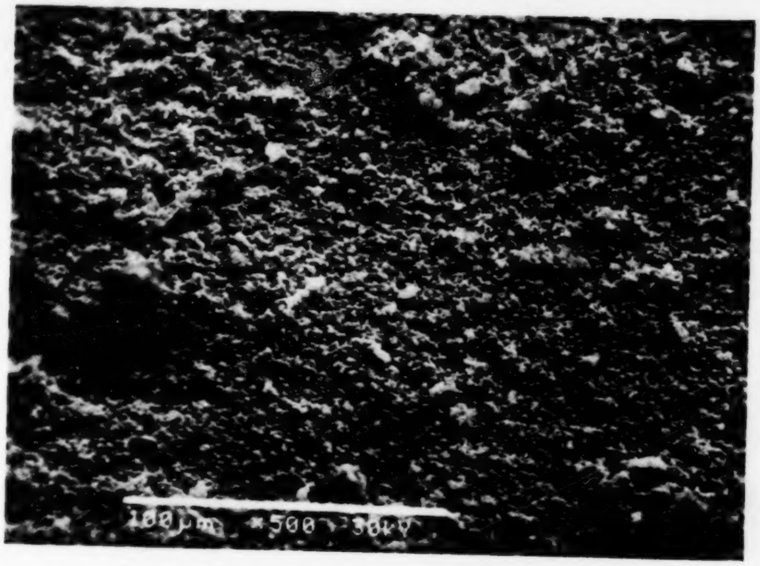
100μm ×500 30kV

Figure E-12. Micrograph of 310-1-A (500X)

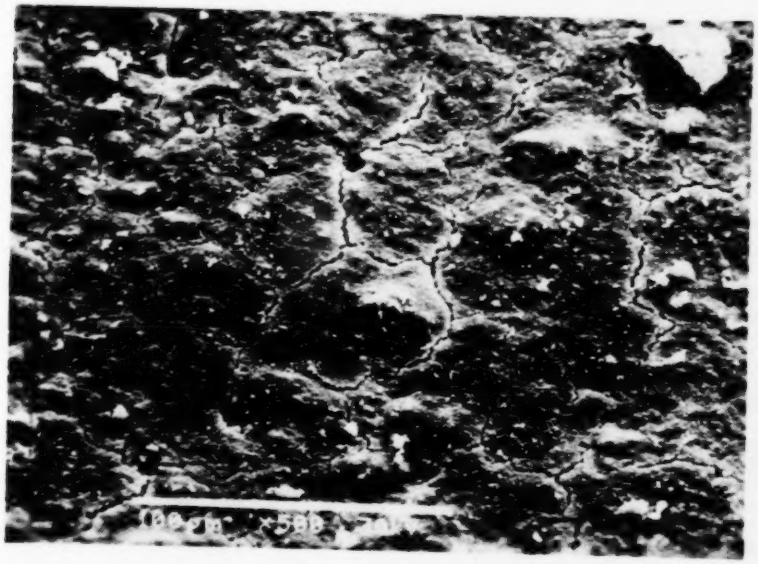
100μm ×500 30kV

Figure E-13. Micrograph of 310-1-B (500X)

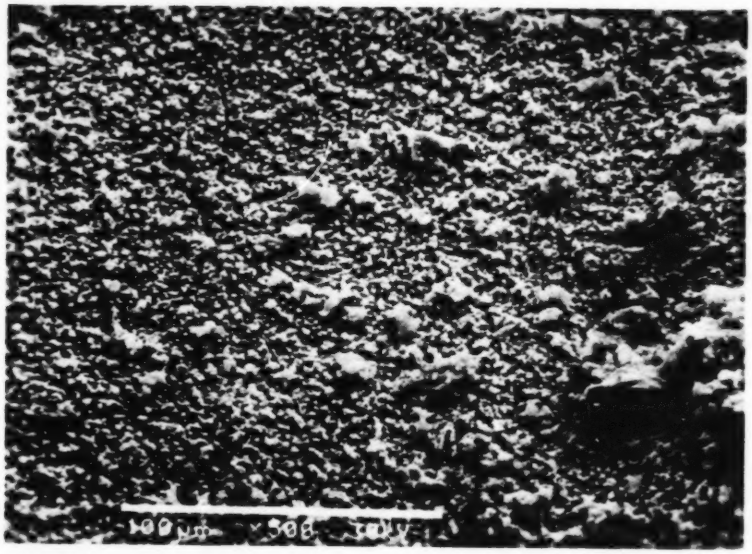
100µm ×500 30KV

Figure E-14. Micrograph of 310-2-A (500X)

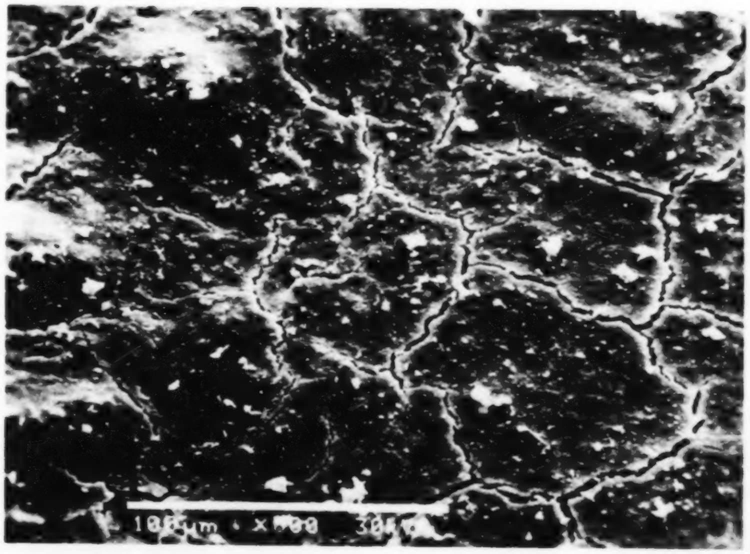
100µm ×500 30KV

Figure E-15. Micrograph of 310-2-B (500X)

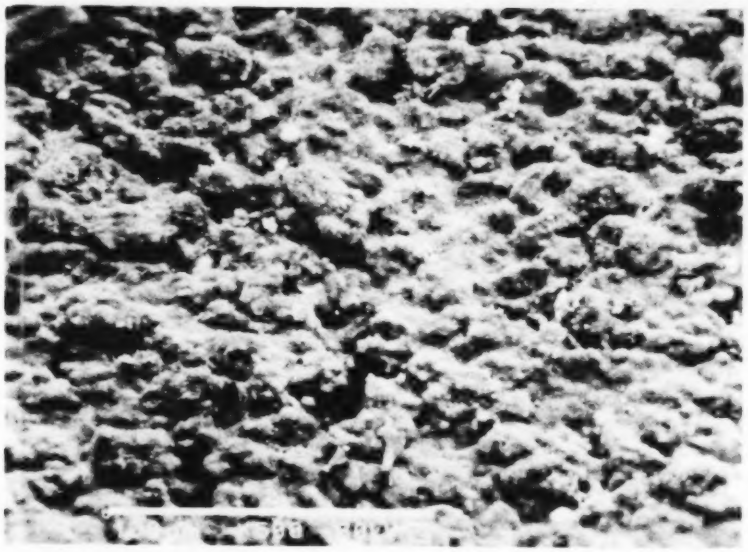

Figure E-16. Micrograph of 312-A (500X)

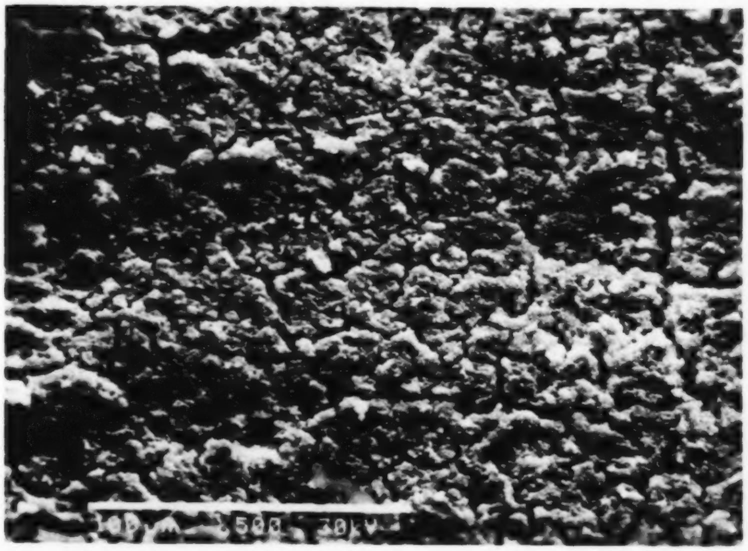

Figure E-17. Micrograph of 312-B (500X)

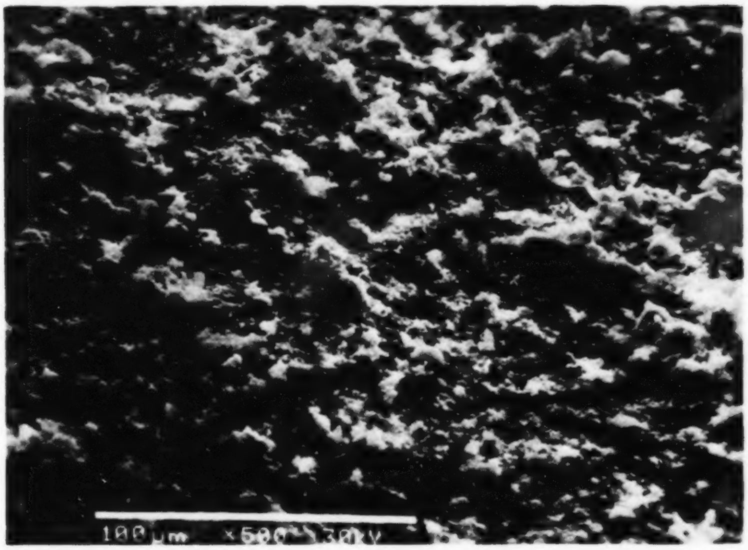
100µm ×500 30kV

Figure E-18. Micrograph of 941-A (500X)

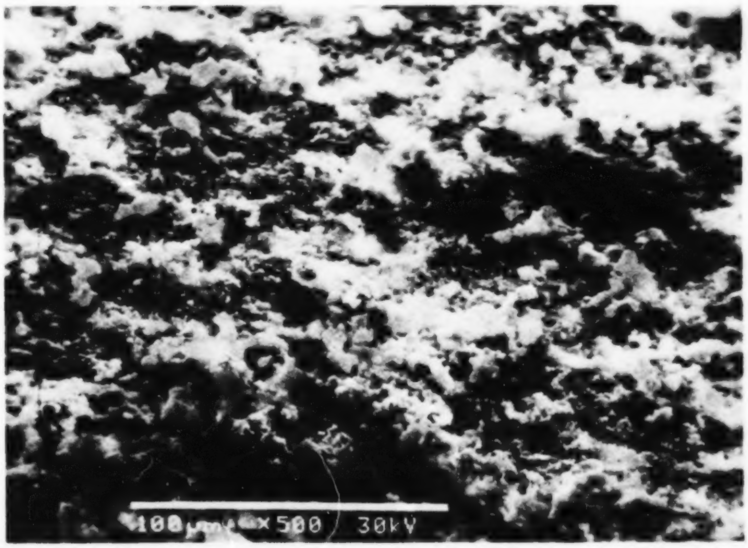
100µm ×500 30kV

Figure E-19. Micrograph of 941-B (500X)